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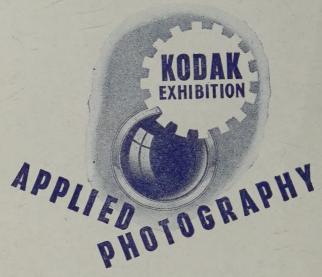
METALLURGICAL ABSTRACTS



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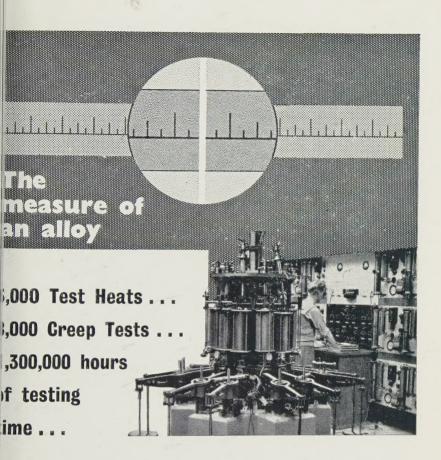
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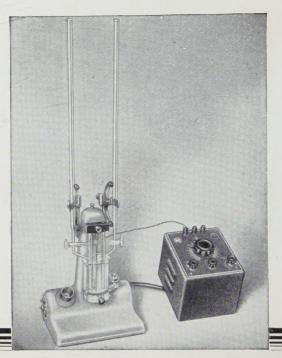
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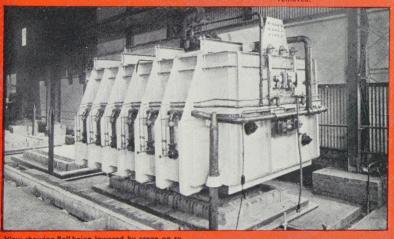
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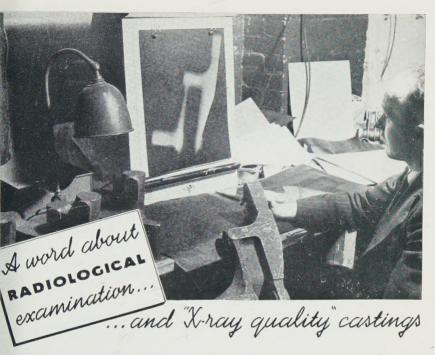
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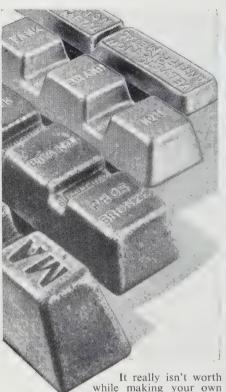
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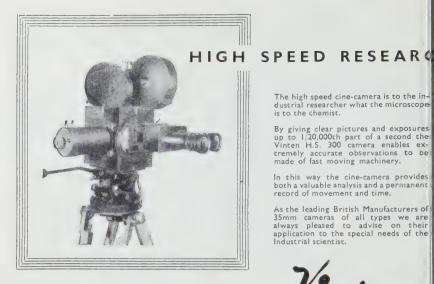
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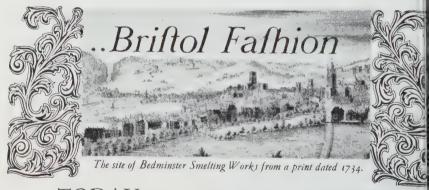
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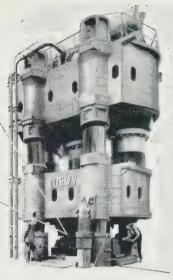
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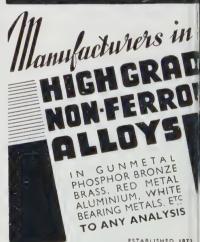
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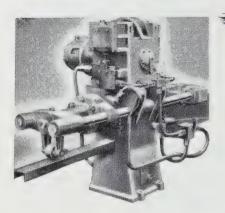
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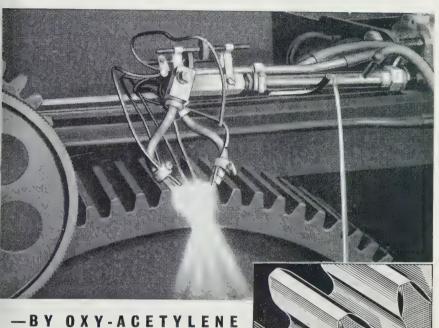
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INSTITUTE NEWS AND ANNOUNCEMENTS

SYMPOSIUM ON INTERNAL STRESSES IN METALS AND ALLOYS. LONDON, 15 AND 16 OCTOBER 1947

As previously announced, and as detailed in a circular which has been sent to all members, the Institute has organized a symposium on "Internal Stresses in Metals and Alloys" to be held on 15 and 16 October 1947 in the Hall of the Institution of Mechanical Engineers, Storey's Gate, Westminster, London, S.W.I. The meeting has been arranged in association with the Faraday Society, Institute of Physics, Institution of Mechanical Engineers (and its Automobile Division), Iron and Steel Institute, Physical Society, and Royal Aeronautical Society.

The object of this symposium—for which the Institute's Metal Physics Committee is responsible—is to bring together engineers, metallurgists, and physicists to discuss problems of common

interest.

The 36 papers contributed to the symposium are available, bound in a paper cover, as a special "advance copy" issue (price 5s. each) for the purpose of stimulating discussion. Later, the papers, together with a full report of the discussions, will be published as Monograph No. 5, for wide distribution. Because of the present paper shortage, it is particularly requested that those who are unable to attend the symposium will await the publication of the cloth-bound Monograph.

The meeting is open (free) to all who are interested in the subject, but attendance at the buffet luncheons and the conversazione arranged in connection with the symposium is limited to members

of the Institute and of the associated societies.

Authors of papers included in this symposium will not present their papers in person, but the discussion relative to each session will be opened by a Rapporteur, who will briefly review the papers allotted to his Section, and may also direct attention to points bearing on the subject of his Section that are included in other papers in the programme. The Rapporteurs may also indicate those points on which they consider that discussion will be most profitable.

It will greatly assist the Chairmen of the Sessions if those taking part in the discussions will confine their remarks to the

specific subject under discussion.

Programme

Wed., 15 Oct., 1947.

10 a.m. to 12 noon. Introductory Address by Colonel P. G. J. Gueterbock, C.B., D.S.O., M.C., T.D., D.L., J.P., M.A., A.D.C., President.

Section I.—The Measurement of Internal Stresses. Chairman: Dr. C. Sykes, F.R.S.; Rapporteur: Mr. D. A. Oliver, M.Sc.

12.30 p.m. Buffet luncheon (price 6s.) at the Institution of

Mechanical Engineers.

2 p.m. to 5 p.m. Section II.—The Origin, Control, and Removal of Internal Stresses. Chairman: Professor L. Aitchison, D.Met., B.Sc.; Rapporteur: Professor H. O'Neill, D.Sc., M.Met.

8 p.m. Conversazione at 4 Grosvenor Gardens, London,

S.W.T.

Thurs., 16 Oct., 1947.

10 a.m. to 12 noon. Section III.—Effects Associated with Internal Stresses: (a) Effects on a Microscopic and Sub-Microscopic Scale. Chairman: Dr. Maurice Cook: Rapporteur: Dr. A. G. Quarrell.

I p.m. Buffet luncheon (price 6s.) at the Institution of Mech-

anical Engineers.

2.30 p.m. to 5 p.m. Section III.—Effects Associated with Internal Stresses: (b) Effects on a Macroscopic Scale, Chairman: Dr. H. J. Gough, C.B., M.B.E., F.R.S.; Rapporteur: Dr. N. P. Allen, M.Met.

Papers

Section I.—The Measurement of Internal Stresses.

"Mechanical Methods for the Measurement of Internal Stresses". by H. Ford, Wh.Sc., Ph.D. (British Iron and Steel Research Association, London).

"The Investigation of Internal Stresses by Physical Methods Other than X-Ray Methods", by R. King, B.Sc. (Metallurgy Department, Royal Aircraft Establishment, Farnborough).

"Measurement of Internal Stresses by X-Rays", by D. E. Thomas, M.A., B.Sc. (Principal Scientific Officer, Armament Research Department, Ministry of Supply, Woolwich).

"Some Fundamental Aspects of the Application of X-Rays to the Study of Locked-Up Stresses in Polycrystalline Metals" by W. A. Wood, D.Sc. (Senior Research Fellow, Baillieu Laboratory, University of Melbourne, Australia).

"The Principles of the Interpretation of X-Ray Photographs of Imperfect Crystals", by H. Lipson, D.Sc., M.A. (Head of the Physics Department, College of Technology, Manchester).

Section II.—The Origin, Control, and Removal of Internal Stresses.

(a) Origin.

"Classification and Nomenclature of Internal Stresses", by E. Orowan, Dr.-Ing., F.R.S. (Cavendish Laboratory, Cambridge University).

"László's Papers on Tessellated Stresses: A Review", by F. R. N. Nabarro, M.B.E., M.A., B.Sc. (Royal Society Warren Research Fellow, H. H. Wills Physical Laboratory, University

of Bristol).

"The Relation of Composition to Stress-Corrosion Cracking in Copper Alloys", by Maurice Cook, D.Sc., Ph.D. (Director, Imperial Chemical Industries, Ltd., Metals Division, Witton, Birmingham).

"Internal Stresses in Steel Castings", by H. Elliss, B.Met., Ph.D. (Chief Metallurgist, K. and L. Steelfounders and

Engineers, Ltd., Letchworth, Herts).

"The Stresses in Large Masses of Steel Cooling from the Austenitic Region", by J. E. Russell, M.A. (Research Department, English Steel Corporation, Ltd., Sheffield).
"Stress in Electrodeposited Metals", by A. W. Hothersall,

M.Sc.Tech. (Armament Research Department, Woolwich).

"Residual Stresses Due to Welding," by R. Weck, Ing. (Department of Engineering, Cambridge University).

"Internal Stresses Produced by the Sliding of Metals", by F. B. Bowden, Sc.D., Ph.D., and A. J. W. Moore, B.Sc. (Department of Physical Chemistry, Cambridge University).
"Some Internal Stresses in Turbine Rotors", by M. C. Caplan,

B.Sc., L. B. W. Jolley, M.A., and J. Reeman, B.Sc. (Research Laboratories, The General Electric Company, Ltd., Wembley).

"Residual Stresses in Beams After Bending", by G. Forrest, B.Sc. (Senior Research Engineer, Aluminium Laboratories,

Ltd., Banbury).

"Internal Stresses in Glassware", by W. C. Hynd, M.Sc. (Physicist, Development Section, Chance Brothers, Ltd., Smethwick, nr. Birmingham).

(b) Control and Removal.

"The Relief of Internal Stresses in Aluminium Alloys by Cold Working", by W. Betteridge, B.Sc., Ph.D. (late of the Bristol Aeroplane Company, Ltd., Filton, Bristol; now at The Mond Nickel Company, Ltd., Birmingham).

"Stress Relief Treatment of Iron Castings". Report of Sub-Committee T.S. 17 of the Technical Council of the Institute

of British Foundrymen.

"Stresses Induced by the Shot-Peening of Leaf Springs", by J. C. W. Humfrey, O.B.E., M.Sc., M.Eng., B.A. (Riley, Harbord, and Law, London; formerly S.T.A.M., Ministry of Supply).

"The Production of Favourable Internal Stresses in Helical Compression Springs by Pre-Stressing", by D. G. Sopwith, B.Sc.Tech. (Senior Principal Scientific Officer, Engineering Division, National Physical Laboratory, Teddington).

"Autofrettage", by A. G. Warren, M.Sc. (Armament Research

Department, Ministry of Supply, Woolwich).

Section III.—Effects Associated with Internal Stresses.

(a) Microscopic and Sub-Microscopic Effects.

"Effects Associated with Stresses on a Microscopic Scale", by Sir Lawrence Bragg, O.B.E., Sc.D., F.R.S. (Cavendish Laboratory, Cambridge University).

"Internal Stresses Arising from Transformations in Metals and Alloys", by Professor F. C. Thompson, D.Met., M.Sc.

(Professor of Metallurgy, Manchester University).

"A Note on the Effect of Internal Stresses on the Rates of Transformation in Iron-Nickel Alloys", by C. C. Earley, B.Sc. (Metallurgy Division, National Physical Laboratory, Teddington).

"Diffusion and Precipitation in Alloys", by F. R. N. Nabarro, M.B.E., M.A., B.Sc. (Royal Society Warren Research Fellow, H. H. Wills Physical Laboratory, The University, Bristol).

"Note on the Effect of Cold Work on the Rate of Precipitation in Aluminium-7% Magnesium and Aluminium-8% Magnesium-1% Zinc Alloys", by E. C. W. Perryman, B.A. (Investigator, British Non-Ferrous Metals Research Association, London). "Age-Hardening", by Marie L. V. Gayler, D.Sc. (Consultant,

British Non-Ferrous Metals Research Association, London; formerly Metallurgy Division, National Physical Laboratory).

"Internal Stresses and the Formation of Hair-Line Cracks in Steel", by Professor J. H. Andrew, D.Sc. (Professor of Metallurgy, University of Sheffield), and Hsun Lee, Ph.D. (Senior Research Assistant, The University, Sheffield). "The Experiments of Boas and Honeycombe on Internal Stresses

Due to Anisotropic Thermal Expansion of Pure Metals and Alloys ", by F. P. Bowden, Sc.D., Ph.D. (Department of Physical Chemistry, Cambridge University).

"A Photoelastic Approach to Stress Modifications Caused by Inhomogeneities", by B. Sugarman, M.Sc., D.I.C. (B.S.A. Group Research Centre, Sheffield).

(b) Macroscopic Effects.

"Influence of Residual Stress on Chemical Behaviour", by U. R. Evans, Sc.D., M.A. (Reader in the Science of Metallic Corrosion, Cambridge University).

"Chemical Manifestations of Internal Stress", by F. H. Keating (Imperial Chemical Industries, Ltd., Billingham Division,

Billingham, Co. Durham).
"Note on Stress-Corrosion Cracking of Steels in the Presence of Sulphur Compounds", by W. P. Rees, M.Sc. (Senior Principal Scientific Officer, Metallurgy Division, National Physical Laboratory, Teddington).

"Internal Stresses in Railway Materials", by Professor H. O'Neill, D.Sc. M.Met. (Professor of Metallurgy, University College, Swansea; formerly Chief Metallurgist, L.M.S. Railway,

Derby).

"Delayed Cracking in Hardened Alloy Steel Plates," by E. H. Bucknall, M.Sc. (The Mond Nickel Company, Ltd., Birmingham), W. Nicholls, B.Sc. (formerly Research Metallurgist, The Mond Nickel Company, Ltd., Birmingham), and L. H. Toft, B.Sc. (The Mond Nickel Company, Ltd., Birmingham).

"The Stress System Causing Hard-Zone Cracking in Welded Alloy Steels", by J. A. Wheeler, Ph.D. (Department of

Metallurgy, The University, Birmingham).

ANNUAL GENERAL MEETING 1948

The dates arranged for the next Annual General Meeting, which will be held in London, are Wednesday, 17 and Thursday, 18 March 1948. If it is found necessary to provide additional time for the discussion of papers, the meeting will commence on Tuesday, 16 March.

MEMBERSHIP ADDITIONS

The undermentioned 13 Ordinary Members and 7 Student Members were elected on 9 September 1947:

As Members

- Alexander, Martin, B.Sc., Metallurgist, Ministry of Supply, Department of Atomic Energy, Risley, Warrington, Lancashire.
- Barr, William, A.R.T.C., Executive Director and Chief Metallurgist, Colvilles, Ltd., Motherwell.

 Bever, Professor Michael B., Sc.D., Assistant Professor, Depart-
- Bever, Professor Michael B., Sc.D., Assistant Professor, Department of Metallurgy, Massachusetts Institute of Technology, Cambridge 30, Mass., U.S.A.
- Cambridge 39, Mass., U.S.A.
 EASDALE, Robert Muir, Metal Merchant and Refiner, 67 Washington
 Street, Glasgow, C.3.
- Street, Glasgow, C.3.
 HANDS, Charles Henry, Chief Chemist, Hoover, Ltd., Perivale, Greenford, Middlesex.
- LACOMBE, Paul Jean Gilbert, Dr. es Sci., Laboratoire Central des Traitements Chimiques, Centre National de la Recherche Scientifique, Vitry-sur-Seine, France.
- McLean, John Campbell, Superintendent-in-Charge, H.M. Assay Office, H.M. Mint, Strand Road, Calcutta, India.
- Murray, Herbert Spencer Stanley, Managing Director, Electroplaters, Ltd., and associated companies, 31 Townsend Street, Glasgow, C.4.
- Murray, Stanley Alexander James, Analytical Chemist; Director, Electroplaters, Ltd., and associated companies, 31 Townsend Street, Glasgow, C.4.
- ROBERTS, Samuel Thomas, Chemical Engineer, International Corrodeless, Ltd., Lockfield Avenue, Enfield, Middlesex.
- RUIMONTE, Professor Dr. Florentino Gomez, Profesor de Quimica Aeronáutica, Departamento de Materiales y Talleres, Instituto Nacional de Técnica Aeronáutica, Narvaez 59, Madrid, Spain.
- WHITELEY, Hubert Augustus, Technical Officer, National Association of Drop Forgers and Stampers, 245 Grove Lane, Handsworth, Birmingham.
- WILLIAMS, Urias, Chief Research Officer, Richard Thomas and Baldwins, Ltd., Light Alloys Section, Briton Ferry, Neath, Glamorganshire.

As Student Members

- Bennett, Bruce Boyd, Chemist, Metropolitan Gas Company, Melbourne, Vic., Australia.
- Butler, Ronald, B.Met., Research Metallurgist, Research Laboratories, British Aluminium Company, Ltd., Chalfont Park, Gerrards Cross, Buckinghamshire.

CHRISTIAN, John Wyrill, B.A., Research Assistant, Inorganic Chemistry Laboratory, Oxford.

Coles, Bryan, B.Sc., Research Assistant (Ministry of Supply) at Oxford University.

Salamy, Stanley George, University of Melbourne, Vic., Australia. Steinberg, Morris Albert, Graduate Student of Metallurgy, Massachusetts Institute of Technology, Cambridge 39, Mass.,

THOMPSON, David Laurance, 98 Acre Lane, Bramhall, Stockport,

Cheshire.

PERSONAL NOTES

- Mr. K. V. Aiyer, B.A., is now in Canada. His address is c/o The Aluminium Company of Canada, Shawinigan Falls, Que., Canada.
- MR. R. W. BERRIMAN has left London and is now with the Australian Aluminium Company Pty., Ltd., Granville, Sydney, N.S.W., Australia.
- MR. W. C. COPPINS has been awarded the M.Sc. degree of London University.
- Dr. H. J. Gough, C.B., M.B.E., F.R.S., has been honoured by receiving the award of the United States Medal of Freedom with Silver Palm. The presentation was made in London on 21 August 1947. The citation, which was read at the ceremony, was: "Doctor Herbert John Gough, United Kingdom, during the period of active hostilities in World War II, performed exceptionally meritorious service in the field of scientific research and development. An engineer-scientist and leading authority on strength of materials, as Director-General of Scientific Research and Development in the Ministry of Supply, he was responsible for much of the British programme for development of ground force weapons, actively co-operating in establishing and supporting throughout the war arrangements for the Anglo-American exchange of important relevant information."
- MR. G. H. HALE is now Assistant Foundry Manager, Frederick Newman and Company, Ltd., Lever Street, Wolverhampton.
- Mr. G. Hoyle, B.Sc., has left Leeds University and has taken up an appointment with the British Iron and Steel Research Association.
- MR. D. M. Lewis, B.Sc., has taken up an appointment with the British Iron and Steel Research Association, Physics Laboratories, Battersea Park Road, London, S.W.II; he is in charge of high-frequency heating work.
- MR. D. McLean, B.Sc., is now at the Metallurgy Division, National Physical Laboratory, Teddington.
- Mr. G. J. Metcalfe, M.Sc.Tech., has joined the staff of the Fulmer Research Institute, Ltd., Stoke Poges, where he is in charge of work on corrosion.

Mr. T. F. Pearson, M.Sc., has left Colvilles, Ltd., and is now with the Consett Iron Company, Ltd., Consett, Co. Durham.

MR. J. S. RODGERS, of the Wolverine Tube Division of the Calumet and Hecla Consolidated Copper Company, Detroit, arrived in England on 25 July and plans to return to the United States in the Queen Elizabeth on 11 October. He is visiting a number of British metallurgical plants.

Dr. Carl H. Samans has been appointed Chief of the Metallurgical Section, Research Laboratory, American Optical Society, Southbridge, Mass., U.S.A., replacing Mr. W. J. Wrighton, who has retired after holding the position for 27 years.

Dr. C. J. SMITHELLS is on a visit to the United States.

Mr. P. Vajragupta, B.Sc., A.R.S.M., has left London and is now at the Government Mines Department, Bangkok, Siam.

DEATH

The Editor regrets to announce the sudden death, on Wednesday, 10 September 1947, of Mr. P. W. ROLLESTON, B.A., Vice-President of Aluminium Laboratories, Ltd., Banbury, Oxon.

LOCAL SECTIONS NEWS

PROGRAMMES FOR THE SESSION 1947-48

Programmes already arranged are detailed below. Members are reminded that (free) membership of the Local Sections is a privilege of membership of the Institute and that those who desire to receive notices of Local Section meetings must notify the responsible Honorary Secretary to that effect.

Birmingham.

1947.

Dr. G. Schlesinger: "Machinability". Thurs., 25 Sept.

Mr. F. E. Stokeld: Presidential Address to Thurs., 2 Oct. the Birmingham Metallurgical Society.

Open Discussion: "The Significance of Mechanical Testing". Thurs., 23 Oct.

Dr. G. V. Raynor, M.A.: "The Determina-Thurs., 6 Nov. tion of Constitution Diagrams".

Mr. W. E. Ballard: Film on "Metal Spraying" and talk on "Protective Coatings". Thurs., 27 Nov.

Students' Evening. Thurs., 4 Dec. XXXV

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1948.

Symposium on "Chain Making". Thurs., 22 Jan.

Dr. W. Steven: "Modern Developments in Hardenability Testing". Thurs., 5 Feb.

Mr. C. A. H. Jahn: "The Metallurgy of Gold, r. C. A. H. Jann.
Silver, and Platinum".
Silver, and Platinum".
Casting " Thurs., 26 Feb.

Mr. F. Hudson: Thurs. 4 Mar. (illustrated by a film).

Mr. L. F. Denaro: "The Metallurgy of Alloy Thurs., 25 Mar. Steel Welding ".

Special meeting of the Local Section. Thurs., 22 Apr.

All meetings take place in the Lecture Hall of the James Watt Memorial Institute, Great Charles Street, Birmingham, at 6.30 p.m. The programme is arranged jointly by the Midland Metallurgical Societies, comprising—in addition to the Local Section of the Institute of Metals—the Birmingham Metallurgical Society and the Staffordshire Iron and Steel Institute.

The Honorary Secretary of the Local Section is Mr. E. H. Bucknall, M.Sc., 53 Halesowen Road, Quinton, Birmingham 32.

London.

1947.

Mr. E. H. Bucknall, M.Sc.: "The Hardening Thurs. 9 Oct. of Non-Ferrous Alloys and Steels".

Professor C. W. Dannatt, A.R.S.M., D.I.C.: "Some Aspects of Metal Refining" (at the Thurs., 13 Nov. Royal School of Mines, South Kensington, S.W.7).

Fri., 5 Dec. Annual Dance, at 4 Grosvenor Gardens, London, S.W.I.

Mr. G. Skript, Dipl.-Ing.: "The Mechaniza-Thurs., 11 Dec. tion of Non-Ferrous Metal Foundries" (Joint Meeting with the London Branch of the Institute of British Foundrymen, at the Waldorf Hotel, Aldwych, W.C.2, at 7 p.m.)

1948.

Thurs., 8 Jan. Dr. L. B. Hunt, M.Sc.: "Silver".

Dr. H. Sutton: "Metallurgical Problems of Importance in Aircraft". Thurs., 12 Feb.

Major C. J. P. Ball, D.S.O., M.C.: "The Mon., 1 Mar. Manufacture and Usage of Magnesium and its Alloys". (Joint Meeting with the London Section of the Society of Chemical Industry, at the Rooms of the Chemical Society, Burlington House, Piccadilly, W.I. at 6.30 p.m.).

Annual General Meeting (6 p.m.); Open Discussion on "The Oxidation of Metals" Thurs., 8 Apr. (7 p.m.). The subject will be introduced by short papers by Professor N. F. Mott, M.A., F.R.S., and Dr. J. H. Mitchell.

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Except where stated otherwise, the meetings will be held at

4 Grosvenor Gardens, S.W.1, at 7 p.m.

The Honorary Secretary of the Local Section is Dr. E. C. Rhodes, c/o The Mond Nickel Company, Ltd., Development and Research Department, Bashley Road, London, N.W.10.

Scottish.

1947.

Mon., 13 Oct. Mr. G. L. Willan: "The Design and Use of Electric Melting Furnaces in the Non-Ferrous Industry".

Mon., 10 Nov. Mr. A. Craig MacDonald, B.Sc.: "Commentary on a Visit to America".

Mon., 8 Dec. Mr. R. E. Wilson: "Electroplating Practice and Engineering Application".

The meetings are held at the Institution of Engineers and Shipbuilders in Scotland, 39 Elmbank Crescent, Glasgow, C.2, at 6.30 p.m. A light snack meal is served before each meeting, from 6 to 6.30 p.m.

The Honorary Secretary of the Local Section is Mr. Matthew

Hay, 132 Elliot Street, Glasgow, C.3.

Sheffield.

1947.

Fri., 31 Oct. Mr. A. W. Hothersall, M.Sc.Tech.: "Electroplating Problems".

Fri., 21 Nov. Mr. A. J. Murphy, M.Sc.: "Magnesium Alloys".

Fri., 19 Dec. Mr. H. Evans, Assoc.Met.: "Surface Finish and Electrolytic Polishing".

1948.

Fri., 23 Jan.

Mr. E. W. Colbeck, M.A.: "Some Metallurgical Problems in the Field of Atomic Energy". Joint meeting, to which members of the Sheffield Society of Engineers and Metallurgists are invited (at the Royal Victoria Hotel, Sheffield, at 6.15 p.m.).

Fri., 20 Feb. Lecture on "Powder Metallurgy" (name of lecturer to be announced later).

Fri., 19 Mar.

Mr. J. F. B. Jackson, B.Sc.: "Centrifugal Castings". Joint meeting, to which members of the Sheffield Section of the National Trades Technical Societies are invited.

Except where otherwise stated, the meetings will be held in the Mining Lecture Theatre, Department of Applied Science, The University, St. George's Square, Sheffield, at 7.30 p.m.

The Honorary Secretary of the Local Section is Dr. W. R. Maddocks, Department of Metallurgy, The University, St. George's Square, Sheffield.

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Swansea.

1947.

Tues., 14 Oct. Mr. W. E. Ballard: "Metal Spraying" (illustrated by a film) (at the Metallurgy Department, University College, Swansea).

Wed., 19 Nov. Sir Arthur Smout, J.P.: "The Place of the Metallurgist in Industry" (at the Guildhall, Swansea).

Tues., 2 Dec.

Dr. R. Higgins, B.Sc., and Mr. D. W. Hopkins, B.Sc.: Accounts of visits to Canada and the United States under the auspices of the Nuffield Foundation Scheme (at the Y.M.C.A., Swansea).

1948.

Tues., 13 Jan. Display of industrial films (at the Metallurgy Department, University College, Swansea).

Tues., 10 Feb. Mr. W. H. Tait: "Bearings" (at the Y.M.C.A., Swansea).

Tues., 9 Mar. Lecture on "Continuous Casting" (at the Y.M.C.A., Swansea).

Tues., 20 Apr. Particulars to be announced later.

The meetings are held at 6.30 p.m.

The Honorary Secretary of the Local Section is Mr. D. W. Hopkins, B.Sc., Metallurgical Department, University College, Singleton Park, Swansea.

OTHER NEWS

ROYAL SOCIETY OF ARTS

H.R.H. Princess Elizabeth has graciously accepted the invitation

of the Royal Society of Arts to become its President.

The Royal Family has been closely connected with the Royal Society of Arts for over a hundred years. Prince Albert became the Society's President in 1843, and in that capacity initiated the Great International Exhibition held in Hyde Park in 1851. Other Royal Presidents have been their Royal Highnesses The Prince of Wales (later King Edward VII), The Prince of Wales (later King George V), and The Duke of Connaught.

The Society is the third oldest of the learned Societies in Britain, and will shortly prepare to celebrate its second centenary

in July, 1954.

REPORTS ON JAPANESE INDUSTRY: INDUSTRIAL STATISTICS

A number of reports on technical intelligence from Japan are being published in the B.I.O.S. series and a token free distribution made to Research and Trade Associations, Universities, Public Libraries, and Professional Societies. It should be emphasized,

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however, that the British Intelligence Objectives Sub-Committee is only authorized to obtain information on processes, &c., developed during the war years and that, therefore, only information falling within this category will be included in the reports.

Certain post-war industrial statistics are, however, now becoming available from American sources, and extracts are being published monthly. These reports will not be given a free distribution, but may be purchased from H.M.S.O. The issues for January and February 1947 are available now, at prices ranging from 1s. 6d. to 2s. 6d. per copy, according to subject.

METAL FINISHING JOURNAL

Electroplating is the title of a new technical monthly dealing with plating, anodizing, enamelling, pickling, lacquering, bronzing, polishing, and phosphating, the first issue of which is scheduled for November. This will be the first British journal to be devoted

exclusively to metal finishing.

The editor will be Mr. C. R. Draper, who has been Editor of Paint Manufacture, and Assistant Editor of The Metal Industry. For the time being he will also be responsible for advertisements and general management. The publishing office is at 83 Udney Park Road, Teddington, Middlesex. The price of the new periodical will be 37s. 6d. per annum.

DIGEST OF ARTICLES ON DIAMONDS

The Industrial Diamond Information Bureau, Industrial Distributors (1946), Ltd., St. Andrew's House, 32–34, Holborn Viaduct, London, E.C.1, publishes monthly a bulletin containing abstracts of articles dealing with properties and industrial applications of the diamond, together with notices of patents and patent applications in many countries. A copy of this bulletin may be obtained, free of charge, on application to the above address.

FORTHCOMING MEETINGS, ETC.

Chemical Society.—Professor F. G. Donnan, C.B.E., D.Sc., LL.D., F.R.S. Ernst Julius Cohen Memorial Lecture. (Burlington House, Piccadilly, London, W.1, Thursday, 2 October 1947, at 7.30 p.m.)

Chemical Society.-Professor E. G. Cox, D.Sc.: "Crystallographic Technique and its Chemical Significance ". (Burlington House, Piccadilly, London, W.1, Thursday, 23 October 1947, at 7.30 p.m.)

Chemical Society (at Edinburgh).—Professor W. Wardlaw, D.Sc.: "Modern Ideas of Valency". (Joint meeting with the Local Sections of the Royal Institute of Chemistry and Society of Chemical Industry, North British Station Hotel, Edinburgh, Thursday, 16 October 1947, at 7.30 p.m.)

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Chemical Society (at Glasgow).—Professor H. Nicol, Ph.D.: "From the Highest to the Lowest". (Joint meeting with the Alchemists' Club and the Andersonian Chemical Society, Chemical Lecture Theatre, Glasgow University, Friday, 31 October 1947, at 3.45 p.m.)

Institute of Welding.—Presidential Address by Mr. J. L. Adam, C.B.E. (Institution of Civil Engineers, Great George Street, London, S.W.1, Wednesday, 29 October 1947, at 6 p.m.)

Swansea and District Metallurgical Society.—Presidential Address by Mr. E. A. Davies. (Royal Institution of South Wales, Swansea, Saturday, 18 October 1947, at 6.30 p.m. Members of the Institute of Metals are invited.)

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THE APPLICATION OF ETCH-FIGURES ON 1108 PURE ALUMINIUM (99.99%) TO THE STUDY SOME OF MICROGRAPHIC PROBLEMS.*

By PAUL LACOMBE,† D.Sc., MEMBER, and LOUIS BEAUJARD,‡ L. es. Sc. (TRANSLATED BY NORMAN STUART, Ph.D.)

Synopsis.

By using an electrolytic polishing method on refined aluminium, it has been possible to develop a method of micrographic attack which reveals etch-figures in a particularly clear manner. The perfection of the geometric form of these figures has enabled a rapid determination to be made of the orientation of the metal crystals from a study of their elements of symmetry.

This has enabled the importance of the relative orientations between adjacent crystals to be related to the nature of the grain boundaries, to the recrystallization due to heat-treatment, and to the mutual plastic deformations of two adjoining crystals. This method of attack has shown, above all, the imperfections in the natural structure of large metal crystals, regardless of the methods by which they are produced, whether by

recrystallization or by slow solidification.

Single crystals of aluminium are, in fact, shown by the polyhedral alignments of the etch-figures to be composed of an aggregate of little crystalline "blocks" whose orientations are very slightly, but perceptibly, different. This mosaic of microscopic blocks constitutes the assemblage into a monocrystal such as is revealed by the classical methods of macrographic attack, and examination of a monocrystal by X-rays has enabled this hypothesis to be confirmed and a determination made of the importance of the disorientations.

I.—Introduction.

In general, it is known that specular polishing, by either mechanical or electrolytic means, for the purpose of a micrographic examination of metals does not itself suffice to elucidate their structure. It is necessary that polishing should be followed by an appropriate attack to reveal, for example, the state of granulation. The actions of these micrographic reagents differ according to their concentrations and composition, and in the case of a pure and homogeneous metal one may either observe a uniform dissolution of the crystals constituting the polycrystalline aggregate, or a preferential attack of the intercrystalline coundaries or even of certain crystals, depending on their orientation.

* Manuscript received 15 July 1946.

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One particular class of reagents has a very localized action on the metal, and is characterized by the formation of etch-figures having geometric forms which depend on the crystallographic orientation of the surface being examined. In this work it is intended to show that the interest of this type of micrographic reagent is not limited merely to a determination of crystalline orientations.

A number of earlier workers had already begun to study etch-figures In particular, the classic work of Osmond and Cartaud 1 should be cited on etch-figures and percussion figures on iron, since the object of their work was to determine what structural modifications were under gone by iron in the course of its allotropic transformations. The more general study made by Portevin in 1923 should also be quoted,2 since which time, etch-figure reagents have been chiefly used for examining the crystalline orientation of large metal crystals by macrographic methods. These are based on the fact that the facets of the etch-figure: are all similarly oriented on the surface of the same crystal and form a system of small mirrors which will reflect a collimated beam of incidenlight in one definite direction. The orientation of the crystal is thus determined by means of the usual crystallographers' goniometer. studies by Weerts, and Barrett and Levenson are examples of this method. In their measurements an attempt was made to increase the number of etch-figures on the same crystal by prolonging the dura tion of the action of the reagent in order to increase the number of small mirrors taking part in the reflection and so increase the brightness of the reflection, and, thus, the precision of the measurement of orientation But the etch-figures then mask one another in such a way that it il difficult to determine their individual elements microscopically. In the present work, however, we have tried to obtain fewer and large etch-figures, the geometric proportions of which enable a microscopic examination to be carried out at all magnifications. Furthermore, we have been able to show that there is not a random distribution or etch-figures on the surface of any given crystal, but that this is related directly to its structure.

It has only been possible to complete this study of the etch-figured by taking advantage of the improvements already developed in micros graphic technique. For a correct interpretation of the results, the characteristics of etch-figures demand an initial surface as perfectly polished as possible. In the preparation of the metal specimens all scratches or pits are liable to modify, by local deformation, not only the form, but also the more or less regular distribution of the etch-figures. It was in this way that Portevin 5 was able to demonstrate, very clearly the influence of local deformations due to polishing scratches, on the

etch-figures on an iron crystal, and was also able to show striations due to an accumulation of figures forming right above the old scratches which had been more or less removed by polishing. We have confirmed that the distribution of etch-figures is also very sensitive to the existence of locally cold-worked regions. In order to do this, we made a deep pinscratch on the surface of a sheet of refined aluminium of coarse grainsize, kept at a temperature of 400° C. In the course of rapid cooling, the most deformed region, corresponding to the centre of the scratch, recrystallized as is shown in Fig. 1 (Plate I), where, on either side of a central band of small crystals corresponding to the bottom of this scratch, the etch-figures which have collected are more or less unorientated and badly formed. It should be mentioned that this observation was made after a slight levelling of the surface had been effected by electrolytic polishing, in order to permit its microscopic examination.

This influence of even a slight cold working on the distribution of the figures demonstrates clearly that any mechanical polishing of the specimens should be forbidden in such a case as the present, because refined aluminium is so soft that it would be difficult to polish it properly without the inclusion of abrasive particles. The new electroytic methods of polishing, however, obviate these difficulties and above all, avoid producing in the surface an amorphous cold-worked layer due to mechanical polishing, which can disturb the crystalline orientation by ts effect on the metal substrate and so alter the form of the etch-figures. Electrolytic polishing is really indispensable in the case of monocrystalline specimens and even in the case of the very large crystals employed in this study. For the depth of the layer disturbed by nechanical polishing is actually greater than that of the amorphous Beilby layer recognized as present in the case of metals having a finer crystal size. In collaboration with Chaudron and Bénard 6 we have recently shown, by the use of X-rays, that on single crystals of aluminium and iron the depth of the disturbance can extend to between 20 and $50 \,\mu$.

Further, by using metals of the greatest possible purity (refined duminium 99.99%, distilled zinc, sublimed magnesium, electrolytic copper, &c.) one prevents that too rapid multiplication of etch-figures which leads to a mutual encroachment, unfavourable to their regular growth. It is clear that the presence of inclusions, or of finely divided undissolved constituents, will also contribute to those accidental defects in the etch-figures which have no visible connection with the true crystal structure.

This work has been mostly devoted to single crystals, or to specimens composed of large crystals of aluminium, refined to a purity of 99.99%,

prepared by Carpenter and Elam's method 7 of "critical deformation", as well as by a new method of fusion which will be the subject of a further paper. Reference will be made, incidentally, to the results obtained with such other metals as copper and zinc and they will be compared with aluminium.

II.—Choice of Reagents Used for Developing Etch-Figures and Methods of Employing Them.

Every etch is preceded by as perfect an electrolytic polishing as possible, for which we have used Jacquet's 8 electrolyte having the composition:

Aluminium specimens are polished directly in this bath without any previous mechanical treatment. Polishing takes place at a potential of between 22 and 25 V., using the potentiometric set-up recommended by Jacquet. In this way it is easily possible to polish large metal surfaces working at a current density of 0.8-2.5 amp./dm.², which is considerably lower than that necessary in the original series circuit 9 (4-6 amp./dm.²)

It is important to note that the perfection of the polishing here obtained determines the subsequent behaviour of the metal towards the reagents used for producing the etch-figures. It is necessary to achieve not only a specular polish on a microscopic scale, but also on a macrographic scale. All macroscopic irregularities on the surface caused by too prolonged polishing must be avoided by constant agitation of the specimen during the electrolytic polishing process.

Micrographic etching must follow this polishing with the shortest possible delay, to avoid the disturbing action of the oxide film which forms very rapidly on electrolytically polished aluminium in contact with the air, as has been shown by Morize, Lacombe, and Chaudron.¹⁰

Finally, it is necessary to chose an appropriate reagent, since its chemical nature and the conditions under which it is used are able to impart to the surface of one and the same crystal, etch-figures of different form, though having a common symmetry. Thus, Mahl and Stranski ¹¹ have recently shown, in the course of a study with the electron microscope, that hydrochloric acid in aqueous or alcoholic solution or a mixture of hydrochloric and hydrofluoric acids, gives etch-figures or aluminium whose facets are parallel to the (100) cube faces. On the other hand, dry gaseous hydrogen chloride preferentially develops

figures with facets which are parallel to the (111) octahedral planes. Barrett and Levenson 4 further describe a reagent for zinc giving facets parallel to the (101r) planes (where r can have very different values). In such an exceptional case one might conceivably have an ambiguity in the determination of the crystalline orientation of the micrographic surfaces from the appearance of an etch-figure, and in the case of single crystals of copper we also observed that the facets were not parallel to the (100) planes. Indeed, attack with a warm 10% solution of ammonium persulphate on a copper surface parallel to a cube face, gives etched figures with the octahedral appearance shown in Fig. 2 (Plate I). In the course of what follows, it will be seen that there is a simple way of determining to which planes the faces of such figures are parallel, namely, by the relative orientation of etch-figures and slip-lines. In order that the determination of these orientations may be as simple as possible, it is best to chose a reagent giving etch-facets parallel to those crystallographic planes having the lowest Miller indices.

Thus, on aluminium, for example, the reagent fulfilling this condition is one containing three acids, namely Tucker's formula 12 which is:

15% fuming HNO₃, 45% pure HCl, 25% distilled water, 15% HF,

while Barrett's and Levenson's formula 4 is:

46% HCl, 15% HNO₃, 10% HF, 26% distilled water.

These reagents, however, are not suitable for the application proposed here, namely, for a microscopic observation of isolated and well formed figures. The above formulæ, in fact, give very numerous etch-figures but all having a small surface, and if one extends the period of attack, the etch-figures tend to overlap instead of being separate on grains having a particular orientation, thus preventing any subsequent interpretation.

A systematic study convinced us that the presence of intentionally added water must be excluded: progressive dilution of the reagent increases the number and diminishes the size of the figures produced. In the same way a study of the action of each one of the acids taken separately has shown that hydrochloric acid is the chief factor in causing localized attack, whilst hydrofluoric acid has a marked tendency towards

a uniform dissolving action. We thus finally adopted the following composition:

47% fuming nitric acid, 50% chemically pure hydrochloric acid, 3% pure hydrofluoric acid.

The purity of these reagents is necessary in order to avoid any secondary electrolytic action due to the presence of any metallic compounds (particularly traces of iron in hydrochloric acid). It is important to work at a low enough temperature (10° C.) to avoid a multiplication of the etch figures, and to allow their growth from isolated points of attack. The length of the attack depends mainly on the temperature and on the perfection of the polishing, and the time varies from 30 sec. to 1 min.

We have also confirmed the possibility of obtaining etch-figures by electrolytic means; C. H. Desch and S. Whyte ¹³ used a 5% NaCl solution for electrolytic attack on brass. Mahl and Stranski ¹¹ have developed etch-figures on pure aluminium by an anodic dissolution in concentrated KCl. We have obtained them on both copper (Fig. 3, Plate I) and on aluminium (Fig. 4, Plate I) in the electrolytic polishing bath, by raising the current density towards the end of the polishing procedure. We have not so far been able to make use of this method of attack on aluminium, however, because the figures so obtained are extremely small and much more irregular than those formed by any chemical treatment (Fig. 4, Plate I).

III.—Application to the Study of the Chemical Anisotropy of Crystals and Their Intercrystalline Boundaries.

Besides etch-figures, the etching agent reveals grain boundaries which are otherwise difficult to recognize on pure, electrolytically polished aluminium. The simultaneous observation of the relative orientation of etch-figures on two adjacent grains indicates that their common boundary is more attacked the greater the difference of orientation that exists between contiguous crystals. Thus, Fig. 5 (Plate II) shows a crystal having triangular etch-figures which seem to be situated in the middle of a single crystal having square figures. In reality, this single crystal consists of several grains of very nearly the same orientation, having boundaries which terminate at the angles of the perimeter of the central crystal. The importance of the intercrystalline region revealed by the reagent thus depends essentially on the respective orientation of adjacent grains. If one assumes with Rosenhain and Ewen ¹⁴ that an intergranular "amorphous cement"

is at the origin of the chemical attack on the boundaries, it is difficult to understand why its intensity should be so different according to the respective orientations of neighbouring grains. Either it must be supposed that the width of the amorphous layer is greater, the greater the difference between the orientation of neighbouring grains, or that there exists at their junction, a transitional structure which is more nearly that of the perfect lattice, the nearer the orientation of the two grains is to one another with the consequent continuation of the lattice planes owing to the approximate parallelism of the two crystals.

It could be argued that the particularly marked appearance of the grain boundaries separating two differently orientated crystals is caused by a change of level in the two neighbouring crystals due, in turn, to their unequal velocity of dissolution, either during electropolishing or in the reagent alone. This, however, cannot be the case because: (i) attack by the three mixed acids reagent is restricted (if not too prolonged) to isolated etch-figures and to the intergranular boundaries, and (ii) the microphotograph (Fig. 5), taken with slightly oblique illumination, does not show any relief comparable to that observed in the case when the electrolytic polishing was carried out at a very low current density, as it appears in Fig. 6 (Plate II). Here one sees a preferential dissolution

of certain crystals, or a so-called "electrolytic engraving".

This particular resistance to chemical attack exhibited by certain grain boundaries has already been pointed out by a number of authors, and originally by Gough. 15 Etch-figures have enabled us to demonstrate that this is a function of the relative orientation of the crystals, and explains the great difficulty which one encounters when trying to determine their average grain-size in a sheet having such an orientated texture. known that cold working by rolling gives rise to a structure having preferential orientations which persist on subsequent recrystallization. The crystallographic elements of this orientated texture vary with the purity of the metal and with the degree of cold working. By a study of the etch-figures we have been able to confirm, in particular, Spillett's 16 X-ray observation that the greatest degree of working produces an orientated texture in the case of aluminium such that the 100) cube face is parallel to the plane of rolling. We have in fact observed a marked predominance of crystals showing square etch-figures n the case of extra pure aluminium which has undergone a degree of cold working of 5.000% ("cube texture (100) [001]").

$$\frac{S_0-S}{S}\times 100\%$$

where $S_0 = initial thickness$ S =final thickness.

^{*} Degree of working is expressed by the formula:

The difference in behaviour of the grain boundaries as a function of the relative orientations of adjacent crystals, also provides an explanation of Snoek's ¹⁷ results on the intercrystalline corrosion of the solid solution FeNi. This alloy, when rolled, gives an orientated recrystallization texture analogous to that of pure aluminium, i.e. having the [001] edge in the direction of rolling, and a (100) face in the plane of rolling. In this "pseudo-single" state of granulation, the alloy completely resists intercrystalline attack at high temperatures by oxygen under reduced pressure. On the other hand, a random equi-axial texture in which the grain boundaries separate crystals having different orientations, undergoes a powerful intergranular attack.

Fig. 7 (Plate II) shows an even more characteristic example of chemical anisotropy observed at times both on crystal surfaces and at their grain boundaries. The difference in the speed of attack is characterized by the more or less numerous occurrences of etchfigures on the various crystalline faces. The enhanced resistance to attack of the surfaces of two grains parallel to the (100) planes (square etch-figures) should be noted, and also the very slight attack on the same boundary, becoming more marked where it separates the crystal parallel to a (100) plane from a pointed crystal containing triangular etch-figures. The difference in the speed of dissolution of the grains according to how they are orientated is even more clearly shown if one prolongs the time of the attack of the three-acids reagent. Fig. 8 (Plate II) shows the appearance of an aluminium sheet! consisting of some large crystals which remained for 30 min. in this reagent. Before the attack, the sheet was of uniform thickness, but now presents a change in level from crystal to crystal of as much as 1 mm. By measuring these at known intervals during the attack, one can thus determine, quantitatively, the degree of anisotropy of the crystalline faces. By still further prolonging the attack, it is possible to isolate completely those crystals which have a surface parallel to the (100) cube face.

In conclusion, these anisotropic phenomena connected with the rate of solution explain the appearance of pinhole corrosion on aluminium in certain surroundings. For it is conceivable that a fine-grained sheet composed, for example, of a texture orientated according to the (100) planes would present a greater corrosion-resistance than a sheet having; a random granulation. However, it should be remembered that an orientated texture is seldom perfect: certain isolated crystals such as those visible in Fig. 5 (Plate II) are embedded in this preferentially orientated structure, but have an entirely different orientation, and, in consequence, will be much more rapidly attacked than the rest. On



. 1.—Influence of Local Cold Working on the Distribution of Etch-Figures on Refined luminium. \times 100; reduced 25% in reproduction.



Fig. 2.—Octahedral Etch-Figures on a Single Crystal of Copper Having Its Surface Parallel to a (100) Face. × 500; reduced 25% in reproduction.



3.—Octahedral Etch-Figures on the me Crystal of Copper Obtained by Electry Polishing. × 750; reduced 25% in production.



Fig. 4.—Etch-Figures on Aluminium by Electrolytic Polishing. \times 1750; reduced 25% in reproduction.

[To face p.8,



Fig. 5.—The Influence of the Relative Orientation of the Crystals on the Appearance of Their Intergranular Boundaries. × 500; reduced 25% in reproduction.



Fig. 7.—Resistance to Chemical Attack of Two Grains Having a Surface Parallel to the (100) Cube Faces. × 500; reduced 25% in reproduction.



Fig. 6.—Anisotropy of Rate of Crystal D solution Appearing in the Course of El trolytic Polishing. × 220; reduced 25% reproduction.



(a) Fig. 8.—Extended Attack on a Coarse-Grain Specimen Confirming the Chemical Ani tropy of the Faces as Revealed by Et Figure Frequency. × 1; reduced 25% reproduction.

(a) 1-minute attack. (b) 30-minute attas



. 9.—Pitting Corrosion on a Sheet aving an Oriented Recrystallization exture. × 2; reduced 25% in reroduction.



11.—Influence of Grain Boundary on the ip-Deformation of Two Adjacent Boundries. \times 750; reduced 25% in reproction.

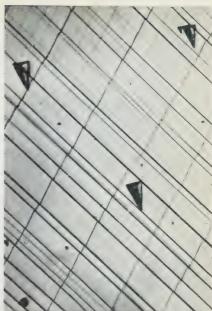


Fig. 10.—Appearance of a Complex Slip on Two Successive Octahedral Planes; Systematic Displacement of the Slip Lines at the Meeting Point with the First System. × 750; reduced 25% in reproduction.



Fig. 12.—Propagation of the Deformation Across the Grain Boundary for Adjacent Grains Having Slightly Different Orientations. × 750; reduced 25% in reproduction.

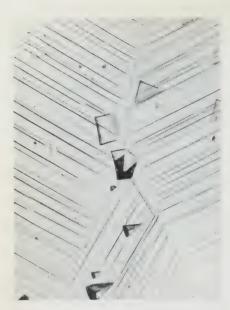


Fig. 13.—Absence of Propagation of Deformation Across Grain Boundaries for Crystals Having Very Different Orientation. × 750; reduced 25% in reproduction.



Fig. 14.—Continuity of the Slip Lines Acrethe Twinning Planes of a Single Crystal Zinc. × 220; reduced 25% in repuduction.

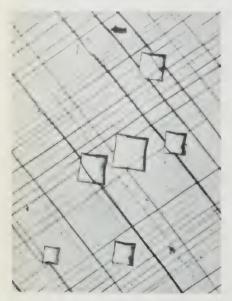
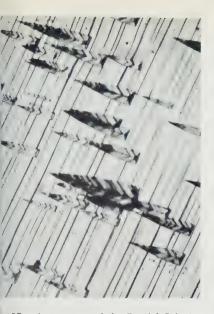


Fig. 15.—Relation Between the Orientation of the Slip Lines of a Crystal Having a Surface Parallel of a (100) Face and the Elements of Symmetry of the Etch-Figures, × 650; reduced 25% in reproduction.



Fig. 16.—Parallelism of the Three Slip Li with the Sides of the Equilateral Et Figures Obtained on a Crystal Surf Parallel to a (111) Plane. × 650; reduce 25% in reproduction.



: 17.—Appearance of the Spatial Orientaion of the Glide-Planes from Their Tracks in the Etched Facets. \times 350; reduced '5% in reproduction.



3. 19.—Extension of the Same Single Crystal at 250°. \times 220; reduced 25% in exproduction.



Fig. 18.—Changed the Orientation of the Slip Lines at a High Temperature; extension of a crystal parallel to a (100) face carried out at 450° after a weaker one at room temperature. × 220; reduced 25% in reproduction.

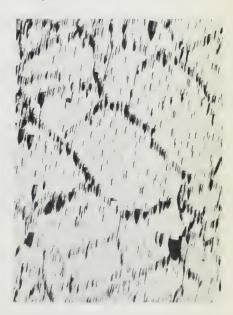


Fig. 20.—Polyhedric Aspect of Alignments of the Etch-Figures on the Surface of the Same Single Crystal. × 100; reduced 25% in reproduction.

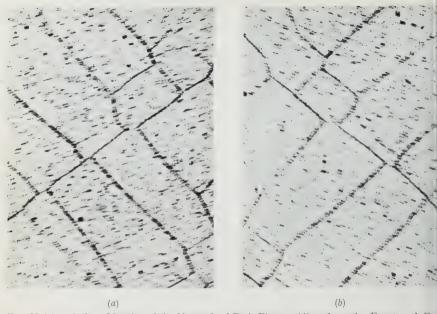


Fig. 21 (a) and (b).—Identity of the Network of Etch-Figures Aligned on the Front and Baof One and the Same Crystal. × 100; reduced 25% in reproduction.

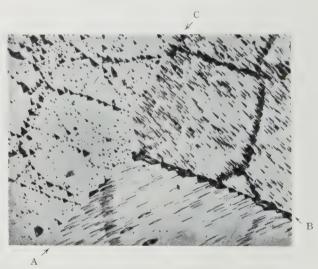


Fig. 22.—Alignments Observed on Three Adjacent Crystals Limited Strictly to the Actual Boundaries (A, B, and C). \times 300; reduced 25% in reproduction.

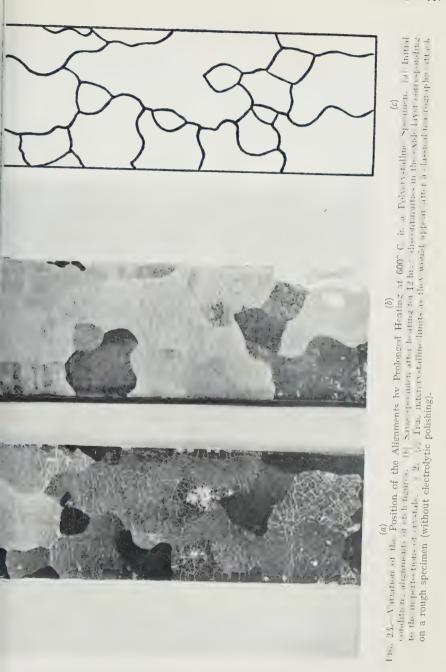




Fig. 24.—Displacement of the Alignments During the Course of Prolonged Heating at 600° C. as Revealed by Atmospheric Oxidation. (A) Original position, (B) final position. × 350, oblique illumination; reduced 25% in reproduction.

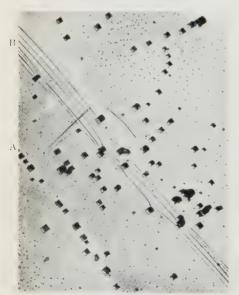


Fig. 26.—Comparison of the Appearance of the Displacement of the Alignments with Those of the Grain Boundaries During the Course of Recrystallization. (A) Original position, (B) final position after heating to 600°. × 220; reduced 25% in reproduction.

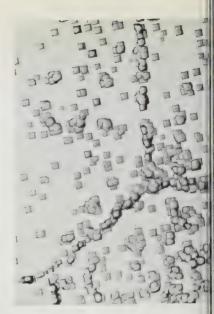


Fig. 25.—Same as Fig. 24 After a New I trolytic Polishing and Etching; iden of the alignment position revealed by a spheric oxidation and by the etch-fig. × 350; reduced 25% in reproduction.



Fig. 27.—Successive Displacement of Grain Boundaries by Recrystallizing During the Course of One and the Strategies at 600° C. × 600; reduced in reproduction.

the macroscopic scale one would therefore have the impression that the sheet had sustained a strictly localized form of pinhole attack corresponding precisely to these particular crystals (Fig. 9, Plate III).

IV .-- A STUDY OF PLASTIC DEFORMATION.

It is known that the simple tensile deformation of a metal generally follows one of two principal mechanisms, e.g. slip and twinning, and these are chiefly determined by the crystal symmetry of the metal. As was first shown by Ewing and Rosenhain, 18 those crystallizing in the cubic system are deformed by a relative sliding along certain crystallographic planes, analogous to cleavage planes, which are the octahedral (111) planes for face-centred metal crystals such as aluminium. 19 After tensile testing of a polycrystalline piece of aluminium, slip bands appear on the surface which are all parallel on any one particular grain, but whose direction varies from one crystal to another according to the different orientations of the crystals in the aggregate and to the general direction of the extension.

In certain crystals, when deformation is continued, new glide-bands appear, parallel amongst themselves but making an angle with the first set of bands which is variable from crystal to crystal. effect is termed "multiple slipping". It is known that the cubic structure possesses 12 equivalent systems of slip; these are the planes and the directions of slip parallel to the faces and to the edges of the octahedron (111). At its commencement, deformation cannot simultaneously occur along all these possible glide systems, and the slip, in fact, starts in the plane and follows the direction where the shear stress is at a maximum, at the same time producing a rotation of the crystal with respect to the general direction of the tensile force. It would be therefore possible to have two simultaneous slips if the crystal happened initially to present two octahedral planes symmetrically disposed with respect to the direction of tension. This case is, however, rarely encountered, so that almost always there are two glides in succession. According to the relative positions of their elements of symmetry, etch-figures thus permit a rapid determination to be made of the direction of tension if there is a possibility of there having been two simultaneous glidings along the octahedral planes. Fig. 10 (Plate III) shows an example of multiple glide in which it is possible to recognize the order in which the slip-lines have appeared. Indeed, one of the systems of slip-lines is quite straight whilst the other suffers systematic displacements, always in the same direction at every intersection with a line of the former system.

It is also interesting to observe the influence of the grain boundaries upon the glide deformation of aluminium. We have shown, in fact, that those of two adjacent grains have not always been entirely independent of one another. Fig. 11 (Plate III) shows two adjacent grains greatly deformed by a tensile force. A change in the direction of the slip-lines is observable as one crosses the grain boundary due to the orientation of the two grains, but the most important point to note is that the slip-lines in each crystal seem to extend, apart from the slight changes in orientation, right across the grain boundary itself. The lines of deformation, in fact, end in every case on one and the same point in the grain boundary. This appears even more clearly if one observes the gliding due to a small deformation: the slip-lines then take on the strictly rectilinear appearance shown in Fig. 12 (Plate III).

Thus, the deformation of each one of the crystals does not appear to be completely independent of that of its neighbour. It seems difficult to assume, therefore, that the boundary of the grains constitutes a frontier, or rather a channel, filled up with amorphous metal, since any such genuine structural discontinuity would oppose a propagation of the deformation. The hypothesis of a "transition-structure" as first put forward by Gough 15 and Hargreaves, 20 and then by Chalmers, 21 in which it is maintained that the atoms are not scattered at random but are in definable positions in the structure appears very plausible. importance of this transitional zone would be greater still, the greater the difference in the orientation of adjacent grains. One can conceive that here the propagation of a system of deformations across the crystal boundaries might be more or less continuous, but where the orientations of contiguous crystals are very different there is no longer any continuity of the slip-lines across the grain boundaries as is shown in Fig. 13 (Plate IV).

It should, however, be possible to compare these facts in the case of the deformation of single crystals of zinc, which show both the phenomena of slipping and twinning. In this case, we observed (Fig. 14, Plate IV), besides the change of orientation of the sliplines on crossing the twins, the same continuity of the slip-lines crossing the twin boundaries, and there can be no question at all here of the presence of amorphous metal in the plane separating the two twins.

We had thought that the use of etch-figures would provide a definite picture of the crystallographic direction on which the deformation by slipping depended. At ordinary temperatures, according to Taylor and Elam, 19 this follows the octahedral (111) planes. This being so, it is sufficient to define the angle formed by the tracks of the (111)

planes on a simple crystallographic plane such as the (100) plane. The orthogonal appearance of the slip-lines in Fig. 15 (Plate IV) does not, however, alone suffice for attributing to the micrographic surface the direction of a (100) plane; there are, indeed, an infinite number of planes on which the tracks of the (111) planes are perpendicular. The use of etch-figures immediately allows us to settle the question. Thus, Fig. 15 shows a crystal where the two systems of slip-lines are more or less rectangular. The etching facets of quaternary symmetry indicate that the surface is indeed one of the (100) planes. It is important to observe that the relative orientation of the slip-lines and the elements of symmetry of the etch-figures is exactly determined. In the case of a single crystal having its surface parallel to a (111) plane (the orientation of which is verifiable by a Laue reflection pattern), one observes that the different systems of slip-lines are exactly parallel to the sides of the equilateral etch-figures (Fig. 16, Plate IV), and these facts provide a concrete confirmation of the octahedral slipping.

It is also possible to locate the position of the glide-planes in space, and to carry out the micrographic attack before the metal is deformed. After pulling a single crystal one observes the tracks of the glide-planes appearing like contour lines on the facets of the etch-figures (Fig. 17, Plate V). It is essential to carry out etching before deformation, or else the etch-figures would have entirely smooth facets. One knows that electrolytic polishing or any micrographic attack on a deformed metal, levels the surface and obliterates all traces of the slip-lines. On the other hand, the need to be able to focus simultaneously on the metal surface and bottom of the etch-pits demands that the latter should be large enough to be visible with a low power objective

having a large depth of focus.

Finally, we have been able to produce evidence of a change in the direction of the slip-plane when a deformation is carried out at elevated temperature. Thus, Schmid and Boas ²² have shown by X-rays that for aluminium heated above 450° C. the slips follow the (100) faces of the cube. Our experiments on the high-temperature testing of monocrystalline test-pieces show that they do not behave in the same way as during cold deformation. In particular, the slip-lines are no longer geometrically parallel when hot. Thus, Fig. 18 (Plate V) shows a single crystal whose surface is perceptibly oriented along a (100) cube face, which was submitted to a slight extension in the cold, followed by another extension at 450° C. In this way one is most easily able to appreciate the difference between the cold and the hot slip-lines: the former are parallel to the diagonals of the square etch-figures, but the latter show a certain degree of deviation or scatter, although there is a

mean direction which is parallel to the sides of the square etch-figures, thus confirming Schmid and Boas's results.

If deformation takes place at temperatures intermediate between 450° C. and room temperature, the slip-lines take on a branched and irregular appearance (Fig. 19, Plate V). This can be explained by assuming that at these intermediate temperatures, the slipping can take place simultaneously on two sets of planes, namely, the (111) and (100) planes. This hypothesis would appear to be confirmed by the fact that one is able to produce a criss-cross pattern of slip-lines in two average directions, respectively parallel to the sides and to the diagonals of the square etch-figures (Fig. 19).

These observations accord with those established by the X-ray work of Andrade and his co-workers,²³ whose experiments led them to the conclusion that in the case of deformation by slipping it is the direction of slip which is the main and independent variable with rising temperature. The direction of slip is always along one of the planes which is perpendicular to the planes of maximum atomic density, while the slipping at higher temperatures is in the zone containing that direction.

V.—Study of the Imperfections in the Structure of Large Crystals of Refined Aluminium.

A controlled 30 sec. attack by the three-acid reagent on refined aluminium sheets of 2 mm. thickness, consisting of several large crystals obtained by Carpenter and Elam's method ⁷ of critical deformation, has enabled us to show a new fact having a direct relation to the internal crystal structure.

Thus, besides the purely chance arrangement of the etch-figures, the reagent produced alignments of figures having a polyhedral appearance on the surface of one and the same crystal (Fig. 20, Plate V). These are not to be attributed to a simple superficial defect in the crystal such as the persistence of local cold work due to a previous scratch, as described by Portevin.⁵ Actually, it is possible after successive electrolytic polishings, taking off substantial thicknesses of metal, to reveal the same pattern of alignments. Furthermore, the back and front of one and the same individual crystal reproduce an identical pattern. This, therefore, demonstrates that these alignments are not due to a surface phenomenon, but show up the surfaces of separation existing throughout the whole thickness of a single crystal, and are of the same category as the grain boundaries in a polycrystalline aggregate. Thus, Fig. 21 (Plate VI) shows clearly that the appearances obtained on the

front and back of one and the same crystal are almost identical, the one photograph being naturally the mirror image of the other. The networks are not exactly similar because the surfaces of separation shown up by them are not necessarily perpendicular to the external surface of the crystal, as is the case also with the genuine grain boundaries.

From the polyhedral appearance of these alignments one might ask whether there is any a priori case for there being old grain boundaries from the first or even the secondary crystallization which are revealing their former traces by reaction with the three-acid etching agent. Such a persistence in the structure as originally cast, or of recrystallization even after the course of later thermal and mechanical treatment, is not rare. We described striking examples of it in the case of aluminium—magnesium alloys obtained by a new micrographic method of attack based on anodic oxidation.²⁴ This "heredity" of structure is more easily to be understood in the case of impure metals, where the impurities are thrown down and accumulated during the course of solidification even at the boundaries of dendritic crystals. This hypothesis cannot be upheld in the present case, however, for the following reasons:

(i) These alignments have been observed on aluminium refined to 99.99% whose extremely low impurity content is incompatible with the continuity of the alignment pattern.

(ii) Examination of several large joined crystals forming a single specimen shows that the alignments stop abruptly at the actual grain boundaries without crossing them (Fig. 22, Plate VI). This shows that they are an inherent property of the actual crystal itself and not the "memory" of an earlier crystallization.

(iii) Single crystals prepared by fusion and slow solidification give rise to an alignment of etch-figures having the same characters as those formed on large crystals prepared by starting from the solid state.

(iv) Whatever the length and kind of subsequent thermal treatments that the large crystals are made to undergo, the retention of a former state of granulation in the metal should remain unchanged. Actually, it is observed that a new heat-treatment completely modifies the alignment pattern as if the monocrystal had undergone a new recrystallization or a reorganization of its structure. Figs. 23 (a) and 23 (b) (Plate VII) show a strip of aluminium 2 mm. thick, 2 cm. broad, and 10 cm. long formed from such large crystals that they reveal macrographic attack. The network of lines is quite observably different after heating for some hours at 600° C.

A further means for showing the existence of these lines is available. If an aluminium specimen, which has previously been polished electrolytically, is heated at 600° C. in the presence of air saturated with water vapour, one observes that the surface of the metal is covered by an opalescent oxide film presenting discontinuities as if the oxide film had sustained shrinkage cracks from having been too violently cooled. This is not the case. We have verified, by renewed polishing and a later attack with the three-acid corrodant, that the apparent discontinuities of the oxide film correspond exactly with the lines on the etch-figures (Figs. 24 and 25, Plate VIII). Examination at a larger magnification shows that the opalescence of the oxide layer formed in the atmosphere is due to the accumulation of very small etch-figures which do not appear in the zone occupied by the main alignment. Thus, Fig. 26 (Plate VIII) shows at the same time an old grouping of etch-figures and the displacement of one by a further heating of the crystal. Apart from the large etch-figures formed by the chemical attack, an accumulation of little pits corresponding to the attack by atmospheric oxidation are observable.

The displacement of the alignments in the course of further heattreatments on single crystals presents an appearance strikingly analogous to the displacement of the boundaries of genuine crystals in the course of corresponding heat-treatments. If an annealed aluminium specimen (which may be fine- or coarse-grained) is re-heated to 600° C., one may note a spontaneous movement of the boundaries of some crystals at the expense of their neighbours. This displacement of the grain boundaries has already been observed by Carpenter and Elam 25 and more recently by Gayler.26 But we have observed a new effect. The displacement seems to be produced, in several stages during one and the same heating. if this is sufficiently prolonged, as in Fig. 27 (Plate VIII), where a multiplicity of grain boundaries is shown. This spontaneous displacement of the boundaries, without previous cold working, cannot be attributed to the growth of certain grains at the expense of others, because of the relative orientations of contiguous crystals. hypothesis, favoured by certain authors, has not been verified by an examination of the etch-figures on adjacent grains.

All these experimental facts led us to think that the alignments were superficial marks of discontinuities separating the little "blocks" of very slight differences in orientation making up the crystal grain itself. We have actually been able, by the use of X-ray back-diffraction diagrams, to observe a difference of orientation of several minutes (15′-30′). Similar effects have already been announced by Bridgman ²⁷ with zinc crystals obtained by melting and slow solidification. Likewise,

Buerger ²⁸ has formulated a "lineage structure" hypothesis as the result of a very complete study of metal crystals formed by melting. The so-called single crystals as evidenced by macrographic attack would have a branched structure: that is to say, a progressive and continuous variation in orientation from the centre of the crystal to the outside.

The characteristics of dendritic crystal growth envisaged by Bridgman and Buerger are particularly favourable for the formation of imperfections in structure: for during the course of solidification the very slight traces of impurities in the metals are thrown down at the extremities of the dendrites. The cause of the existence of imperfections in crystals formed by recrystallization in the solid state, such as we find in the case of pure aluminium, is much more difficult to understand. The fact that even a prolonged heat-treatment neither makes these discontinuities in the structure disappear nor enlarges the average dimension of the meshes that limit them, leads one to suppose that these imperfections of structure constitute an intrinsic and necessary property of the metallic crystal.

VI.—Conclusion.

The systematic application of etch-figures has enabled us to show the very different behaviour of crystals and grain boundaries of aluminium according to their respective orientations.

We have further re-established by micrographic methods, the results earlier obtained by X-rays on the subject of deformation at high temperatures. We have shown the existence of discontinuities or imperfections in the structure of large crystals of aluminium obtained both by melting and by recrystallization. These large crystals are composed of an aggregate of little "blocks" whose orientations are very slightly different and whose dimensions are clearly larger than those of the submicroscopic mosaic structure. The possibility of a relation between these two structures is not excluded.

This study would not have been brought to a conclusion but for the use of extra pure, large aluminium crystals and electrolytic polishing prior to etching.

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ON THE EQUILIBRIUM AND KINETICS OF 1109 ORDER-DISORDER TRANSFORMATIONS IN ALLOYS.*

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SYNOPSIS.

The equilibrium of order-disorder transformations in alloys is described, in the first approximation, by formulæ giving the structural parts of internal energy and entropy as functions of a suitable measure of the degree of disorder. In the second approximation, the influence of fluctuations is taken into account. The calculations are compared with experimental results of measurements on the internal energy of CuZn.

The kinetics of the transformations are described in conformity with simple diffusion phenomena in ranges of temperature sufficiently far below and above the critical point; but in a range on both sides of the critical point the rate of transformation is influenced by a thermodynamic potential barrier. This influence is theoretically described on the basis of the fluctuation theory, and the calculations are compared with results of X-ray measurements on AuCu.

I.—Introduction.

HIS paper gives a concise survey of formulæ developed and used uring experimental and theoretical investigations on order—disorder cansformations carried out in this laboratory during some twenty years, is well as a comparison of these formulæ with experimental results. The aim of our theoretical work has differed in principle from that regun by Bethe and continued by many theoretical investigators. These exestigators start from highly simplified assumptions on the intercetion of neighbouring atoms and try to calculate as generally as easible the corresponding partition function and thermodynamic cuantities, calculations which have proved to be very difficult. In our ork we have avoided such simplifying assumptions on the intercetions, which are doubtful from a physical point of view and have tried to deduce, necessarily in a simplified way, formulæ which can describe the phenomena by means of a few empirical constants. The formulæ betained have been of great help for further experimental investigations.

Most of the formulæ presented here have been discussed in more etail in earlier papers. As, however, some of these papers were ublished during the war and in periodicals not often read by those

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specially interested in the physics of alloys, this survey might be appropriate.

II.—General Thermodynamics of Order-Disorder Transformations.

The order disorder transformations in alloys, the nature of which was established by the investigations of Johansson and Linde ¹ in 1925–27, are, at least in the most important cases, characterized by the existence of a continuous series of conceivable, though not always realizable, intermediate states between the states of full order and full disorder.² The equilibrium state at a given temperature is the state which makes the thermodynamic potential a minimum; and, if there are no variations of concentration, the thermodynamic problem is solved if the thermodynamic potential is known as a function of the temperature and some measure of the degree of order. For a solid, the thermodynamic potential may with very good approximation be represented by the free energy:

$$F = U - TS \quad . \quad . \quad . \quad . \quad (1)$$

where U is the energy, S the entropy (e.g. of a gram atom of the alloy), and T the absolute temperature. U and S are the result partly of the vibrational motion and partly of the structural arrangement of the atoms. Now, it is a general experience that the vibrational and structural parts are to a great extent independent of each other, the vibrational part being dependent on the temperature only. As we are here only interested in variations of the structural arrangement, we may exclude the vibrational parts from our discussion. Thus in (1) F is the structural part of the free energy, and U and S are functions of the degree of order but independent of T.

For a purely thermodynamic description of the transformations, the entropy itself may be chosen as a measure of the degree of disorder. The condition that F has to be a minimum for the state of equilibrium at a given temperature may then be written:

$$\partial F/\partial S = 0$$
,

which according to equation (1) gives:

$$\frac{\partial U}{\partial S} = T \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

Therefore, if U is known as a function of S, it is possible to determine the values of U, S, and F for the equilibrium state of any temperature; and the transformation is fully described from a purely thermodynamic point of view by the relation U = f(S).

As mentioned above, this simple treatment implies that the alloy remains homogeneous at all stages of the transformation. In the general case, the free energy of an alloy system at a given temperature must be considered a function of two variables, the degree of order and the concentration; in addition to homogeneous transformations, cases where an alloy in the equilibrium state is split up into two phases of different concentrations and degrees of order are also to be expected. However, even in such cases the transformation process may appear homogeneous if the changes of concentration are slow in comparison with the changes of order. The present survey will be confined to the treatment of transformations without variations in the concentration of the alloy.

III. -THERMODYNAMIC AND STATISTICAL TREATMENT OF ORDER DISORDER TRANSFORMATIONS IN ALLOYS OF THE TYPE AB.

Though the thermodynamic method outlined above, with the entropy S as a measure of the degree of disorder, may be very convenient as a graphic description of the transformations, it is less useful for analytical treatment. All theoretical models show that the energy U must be a rather complicated function of S, which cannot be described by algebraic functions. For analysis, it is often convenient to express S and U as functions of a third variable. On the basis of a simple theoretical model, the author 3 derived the following formulæ for an alloy of composition AB:

$$S = -R [q \ln q + (1 - q) \ln (1 - q)] . . . (3)$$

and

$$U = R \left[\alpha q (1 - q) + \beta q^2 (1 - q)^2 + \gamma q^3 (1 - q)^3 + \dots \right] . \tag{4}$$

Here S and U are referred to one gram atom of the alloy (the sum of A and B atoms being equal to the number of atoms per gram atom). α , β , γ , &c., are constants, different for different alloys. S and q are mutually connected by equation (3), and q is thus a thermodynamically fully defined measure of the degree of disorder as well as S itself. The advantage of q over S is that the energy U may be given in terms of q in a simple algebraic form.

Equations (3) and (4) were derived by statistical methods from a simple, approximate, theoretical model. This approximate model gives to q a simple physical meaning, and also gives a physical reason for the representation of the energy U by a broken series with the exclusion of higher terms as in equation (4). The atomic lattice of a fully ordered alloy of composition AB may be divided into interpenetrating lattices I and II, one occupied by A-atoms and the other by B-atoms. In a state of incomplete order, only a certain fraction, q, of

the possible positions of lattice I is occupied by A-atoms, the other part (1-q) is occupied by B-atoms. In lattice II, the A- and B-atoms occupy the fractions (1-q) and q, respectively. In order to facilitate a simple statistical deduction of entropy and energy, the model was simplified by the assumption that the arrangement of atoms in each lattice part is a statistically disordered one. With this assumption, equation (3), governing the entropy (S), follows directly from Boltzmann statistics. Equation (4), on the energy, is based on the assumption that the energy of the lattice is built up by forces between neighbouring atoms. If only pairs of nearest neighbours were to be considered, there would be the three types AA, BB, and AB to account for, and all terms in equation (4) would be excluded except the first. The same would be the case even if groups of three atoms were considered. If groups of four or five neighbouring atoms make a contribution to the energy not already accounted for by considering the pairs and groups of three, the second term has also to be taken into consideration. Contributions from groups of six or seven neighbours give the third term and so on. As the forces between the atoms are not known, the constants α , β , γ ... have to be determined by measurement. The most direct way to do this ought to be by suitable calorimetric measurements.

Equations (3) and (4), together with the equilibrium condition (2),

which may also be written

$$\frac{\partial U}{\partial q} - T \frac{\partial S}{\partial q} = 0 \quad . \quad . \quad . \quad . \quad (5)$$

are capable of describing various types of transformation by varying the values of the constants $\alpha, \beta, \gamma \dots$ in equation (4). Fig. 1 shows some examples of these various types, using diagrams in which the structural energy (U), a quantity determinable by experiment, is shown as a function of the absolute temperature, T. U is given in calories per gram atom.

Fig. 1 (a) shows how a positive value of α, the other constants being zero, gives a transformation in which the order ends at a critical temperature with a discontinuity in the heat capacity, dU/dT, but without any discontinuity in U itself. A discontinuity of this kind is said to be of the second order, as distinct from discontinuities of the first order with a jump in U. The special case of a transformation with a discontinuity of the second order described by a single constant a, corresponds to the approximation of Bragg and Williams, which is discussed in section VII. The transformations experimentally studied in the 50% alloys CuZn, AuCu, and CdMg are, however, all in some disagreement with this approximation. They all require large negative values of β in addition to the positive value of α .

Fig. 1 (b), for $\alpha = 1850$ and $\beta = -684$, gives, as is shown in section IV, a first approximation to the case of CuZn. The discontinuity is here still of the second order.

Fig. 1 (c), for $\alpha=2325$ and $\beta=-2250$, corresponds, as is shown in section VI, to the case of AuCu with a discontinuity of the first order. The dotted continuation of the curves of equilibrium on both sides of the discontinuity correspond to relative but not absolute minima of the thermodynamic potential, i.e. to metastable states. The discontinuity appears at 680° K.

The term "discontinuities" of various orders is preferred to the term "transformations" of the first, second, or higher order, which has often been used by recent authors. One reason for this is that it is theoretically possible for the same order-disorder transformation phenomenon in an alloy system to have discontinuities of the first or second order in adjacent ranges of concentration passing continuously from one to the other type when the negative value of the constant B passes the limiting value $\alpha/2$. It does not seem practical to place one part of this transformation in the same class with changes of modifications and melting phenomena, and the other part in the same class with, for instance, ferromagnetic transformations.

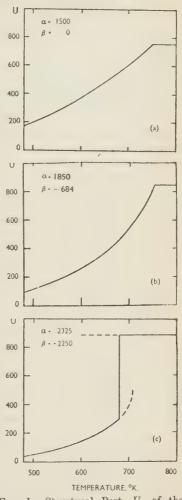


Fig. 1.—Structural Part, U, of the Internal Energy, in Calories per Mol., Versus Absolute Temperature, T.
(a) Approximation of Bragg and Williams; (b) CuZn alloy, first approximation; (c) AuCu alloy.

As mentioned above, the theory of order-disorder transformations given by the three equations (3), (4), and (5), was derived statistically

on the basis of the simplifying assumption of full disorder within each of the two lattice parts. As a consequence of this simplification, we may not expect q, as defined by equation (3), to give exactly the fraction of the two kinds of atom in the lattice parts. Neither are the constants α , β , γ in equation (4) exact measures of the contributions to the energy from groups of two or three, four or five, six or seven, &c., neighbouring atoms. Probably, however, this approximation will have very little influence on the possibility of describing various types of transformation by varied sets of constants α , β , γ

Though the treatment here has been confined to alloys with the composition AB, there is no major difficulty in extending a similar treatment to other stoichiometric or non-stoichiometric compositions.

IV.—The Smoothening of Discontinuities by Fluctuations.

The equations (3), (4), and (5) are only able to describe transformations with sharp discontinuities of the first or second order. From certain investigations, especially the measurements of heat capacity of β -brass by Moser 5 and by Sykes and Wilkinson, 6 we know, however, that order-disorder transformations exist without any sharp discontinuity in the energy U or heat capacity dU/dT. Whether or not there are any discontinuities in higher derivatives is difficult to decide from the measurements available.

This discrepancy between theory and experiment does not mean that equations (3) and (4) should not be able to describe correctly the connection between energy U and entropy S for a given degree of disorder q. The probable cause of the discrepancy is that a fixed value of q has been ascribed to the state of equilibrium, the value making the free energy a minimum. This means that we have assumed the degree of disorder to be the same in all parts of the alloy, and have neglected fluctuations in q, which are apparently not negligible.

The problem of finding a theoretical expression for the energy U as a function of the temperature T, taking the fluctuations fully into account also, would, of course, be solved if it were possible to derive a general expression for the partition function from assumptions about the interatomic forces. As is pointed out in section VII, we are at present very far from a solution of this kind.

There is, however, a certain chance of approaching the experimental U-T curves in two steps, neglecting the fluctuations in the first approximation and taking them into account in the second. The first approximation for an alloy of the type AB is obtained, as described in section III, by choosing the best possible values for the constants α , β , &c., in equation (4).

In order to obtain the second approximation, we first consider the fluctuations in a group of l atoms, l being a number large enough to allow the relations (1), (3), and (4) between U, S, F, and q to be valid within the group. The degree of disorder, q, will fluctuate with the time, giving a distribution function such that the probability of the occurrence of a certain value of q is greater the smaller the corresponding value of the free energy, F.

As the energy, U, of the group also varies with q, U will attain a certain mean value \overline{U} dependent on the distribution function. The theory of fluctuations 7 gives for this mean value:

$$\tilde{U} = \frac{\int_{0}^{0.5} Ue^{-\frac{lF}{RT}} dq}{\int_{0}^{0.5} e^{-\frac{lF}{RT}} dq} \qquad (6)$$

If l is very large, only the ranges near the minima for F give any appreciable contribution to the integrals, and for the limit $l=\infty$ we obtain $\overline{U}=U$, corresponding to our first approximation. If, on the other hand, l is small, the group containing only some hundreds or thousands of atoms; and, if in addition, the minimum of F is rather flat, or if there are two minima of nearly the same height (cf. Fig. 4); the conditions which are fulfilled near the critical points, there might be an appreciable difference between \overline{U} and U. As we know U and F as functions of q and T from the first approximation, we are, in principle, able to compute the mean value \overline{U} for an assumed value of l.

From equation (6) we learn that to obtain the effect of the fluctuations indicated by experimental results, we must calculate with fluctuating groups with rather limited numbers of atoms. As we have no basis for predicting these numbers, the best thing to do is to compute $\overline{U}-T$ curves according to equation (6) for different values of l and then get a rough idea of l by comparison with experiment.

In this way we have found that the results of Sykes and Wilkinson 6 on β -brass (CuZn) may be tolerably satisfied by a constant value of l of about 1200. Fig. 2 shows a collation of theoretical and experimental results. The dotted line gives the U-T curve in the first approximation calculated from equations (3), (4), and (5) with $\alpha = 1850$ and $\beta = -684$. The full line gives the $\overline{U} - T$ curve in the second approximation, calculated from equation (6) with l = 1200. The circles give values computed from the heat-capacity curves published by Sykes and Wilkinson, which were measured with a co-ordinate microscope and integrated graphically. The agreement between theory and experiment is fairly good in the critical range. The discrepancy at low

temperatures is most probably chiefly due to the specimen here not having been in the equilibrium state, which is reached more and more slowly with decreasing temperature. The fact that the alloy of Sykes and Wilkinson did not have the exact stoichiometric composition influences the result in the same direction.

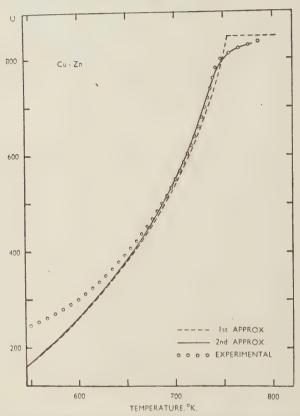


Fig. 2.—Structural Energy, U, for CuZn, in Calories per Mol., Versus Temperature. Comparison of calculated values with experimental results of Sykes and Wilkinson.

The interpretation of this approximate agreement between experimental results and our theoretical formulæ is difficult, and has to be done with great caution. We are not allowed to conclude that the crystal is divided into domains of about 1200 atoms fluctuating independently. Neither may we look upon the value of l as a fixed number. It may well be that l is only an effective mean for a widespread distribu-

tion function. Furthermore, a considerable variation of l with temperature is not excluded. A conceivable interpretation of l, worthy of theoretical investigation, is that l should simply be a lower limit for the number of atoms in groups for which the thermodynamic functions may be defined statistically.

It ought to be mentioned that a theoretical treatment of the fluctuations, somewhat similar to that given here, has been applied by Frenkel, Band, and Mayer and Streeter 10 to melting or condensation phenomena.

Since it has been possible to describe, within, or near to, the limits of experimental error, with only three empirical constants, the rather complicated temperature dependence of the energy content of CuZn over the range where equilibrium states are obtainable, it may finally be emphasized that our approximations appear to be physically sound.

V.—KINETICS OF ORDER-DISORDER TRANSFORMATIONS.

The proper way to obtain knowledge of the kinetics of the transformations has proved to be the study of the ordering process of undercooled disordered alloys (or the disordering of overheated ordered alloys) as a function of time at constant temperature. The study may concern the evolution of heat, the changes of some line on an X-ray photograph, or the variation of electrical resistance or some other physical property. For a comparison of the rate of transformation at different temperatures, one may use either the velocity of change or the inverse function, the time needed for some part of the transformation. In the following short survey, we shall use the half-value time, τ , which is the time necessary for the first half of the change considered.

If the ordering process is an uncomplicated wandering of the atoms to their new positions on the lattice points, i.e. a pure diffusion phenomenon, we may expect the same dependence of temperature as for other diffusion phenomena, and the half-value time τ should approximately satisfy the equation:

Here W divided by the number of atoms in a gram atom is the energy necessary for two atoms to change places, R is the gas constant, and T the absolute temperature. τ_0 is the limiting value of τ at infinitely increasing temperature. Its physical meaning is illustrated by results from AuCu, reported in section VI.

In a range of temperature on both sides of a discontinuity of the first order, there are, however, certain complications which were first

observed 2 as a hysteresis difference between resistance-temperature curves taken at increasing and decreasing temperatures. In connection with the publication of these observations, they were already tentatively interpreted as a result of thermodynamic potential barriers. This idea has been further developed on the basis of a discussion of the fluctuations of order necessary to form stable nuclei of the new state. Although it was suggested that the existence of thermodynamic potential barriers must have a great influence on the fluctuations, it has not yet been possible to establish the condition for a stable nucleus from purely theoretical considerations. It has been necessary to search for this condition in a half-empirical way. For this purpose, investigations on order disorder transformations have proceeded parallel with investigations on the kinetics of precipitation. 11, 12 For the present, the most promising formulation of a condition is that a stable nucleus is received by a fluctuation which makes a group of n neighbouring atoms surmount the top of the potential barrier. The number n has to be determined empirically. With this formulation, one obtains from the fluctuation theory, according to an analysis of Einstein, an additional factor to equation (7) for the half-value time giving the extended expression:

$$\tau = \tau_0 \, e^{\frac{W}{RT}} \, e^{\frac{n\Delta F}{RT}} \quad . \tag{8}$$

where n is the number of atoms in a fluctuating group and ΔF the height of the potential barrier in terms of free energy per gram atom. In ranges of temperature where there is no barrier, the last factor is unity. Taking the natural logarithms of both sides of equation (8) we obtain:

$$\ln \tau = \ln \tau_0 + \frac{W}{RT} + \frac{n\Delta F}{RT} \quad . \quad . \quad . \quad (9)$$

The connection between τ and T is conveniently shown by diagrams with $\ln \tau$ (or $\log \tau$) and 1/T as variables.

VI.—Test of the Theory on Results of X-Ray Measurements on the Kinetics of Transformation in AuCu.

The kinetics of the order-disorder transformation in an alloy with the composition AuCu was studied fairly thoroughly by X-ray investigations by Källbäck, Nyström, and Borelius. The change of certain lines in Debye Scherrer diagrams, the half-value time τ was derived for different temperatures and compared with the predictions of the fluctuation theory. In Fig. 3 the experimental results are plotted ascrosses in a log τ -1/T diagram. The circles on the figure give the results of a renewed calculation according to the formulæ given in the

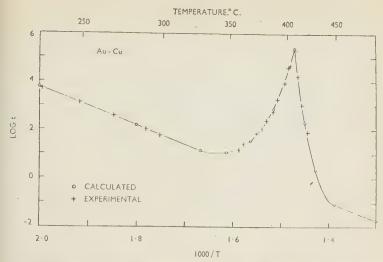


Fig. 3.—Dependence on Temperature of Half-Value Time for the Transitions in AuCu.

foregoing sections, using suitable values of the empirical constants. In order to fit the experiments, equation (9) has to be written:

$$\log \tau = \log 1.1 \times 10^{-12} + \frac{18000 \log e}{T} + \frac{1740 \Delta F \log e}{RT} . \quad (10)$$

where the potential barriers ΔF are obtained graphically from an expression of the free energy:

$$F = R[2325q (1 - q) - 2250q^{2} (1 - q)^{2} + T(q \ln q + (1 - q) \ln (1 - q))] (11)$$

formed in agreement with the equations (1), (3), and (4), where only, the first two terms in equation (4) for the energy are taken into account.

The experimental points in the low-temperature range (200°-300° °C) are located in the diagram on a straight line, determined by the two first terms of equation (10). The slope of this line is W/R = 18,000, a value that is of the same order as the constants obtained from diffusion in copper, gold, and their alloys. The extension of this line cuts the 1/T axis, giving $\tau_0 = 1.1 \times 10^{-12}$. The order of magnitude of this constant is also understandable from a physical point of view. As appears from equation (7), τ_0 is the half-value time of a transformation when the Boltzmann factor is unity, i.e. when there is no energy hindrance for the atoms to change places. In such a case, one could expect about one exchange per atom and period of thermal vibration. This period is

obtained from the Debye characteristic temperature to about 2×10^{-13} sec. The empirical value of the half-value time τ_0 is some five times the period of vibration, which, although there are as yet no detailed theoretical investigations on this subject, seems to be a reasonable result. An ordered arrangement may be obtained from a disordered one with a mean displacement of a few steps per atom.

The deviation of the curve from the straight line between 330° and 440° C. is due to the third term on the right in equation (10). The position, extension, and shape of this deviation are determined by the

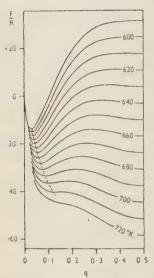


Fig. 4.—Thermodynamic Potential Versus Degree of Disorder for AuCu.

two constants $\alpha = 2325$ and $\beta = -2250$ of equation (11). These constants are obtained by trial. A diagram with F as a function of q, used for graphical determination of the potential barrier ΔF , is given in Fig. 4. The height of the deviation gives the value of the number, n = 1740, of atoms in a fluctuating group producing a stable nucleus. Although we have no theoretical ground for dealing with n as a constant, the result so far gives no reason to assume a dependence of n on temperature. The order of magnitude of n seems reasonable, and n is great enough to justify the statistical background of the last factor in equation (8).

The results of the X-ray investigations on AuCu have also given support in another way to the idea of the influence of thermodynamic potential barriers on transformations. The change of the Debye-Scherrer diagram during the trans-

formation from disorder to order is different in the low-temperature range, where there is no barrier, and in the range of a barrier. The difference is exemplified in Fig. 5 by microphotometer curves for the line (311) for various times of heat-treatment at 290° and 395° C. At 290° C., where according to Fig. 3 there is no barrier, the transformation passes through a continuous series of intermediate states. At 395° C., where the barrier is well developed, the intermediate states, which are statistically improbable, have a relatively short lifetime and are very evanescent in the photometer diagram.

A further test of the theory should be obtained if the energy constants α , β . . ., which are here calculated for AuCu from kinetic data, could

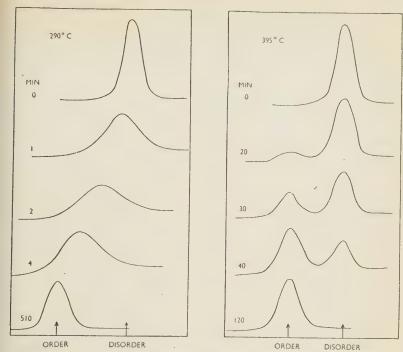


Fig. 5.—Microphotometer Curves for Various Times of Heat-Treatment of AuCu at 290° and 395° C.

be determined independently by calorimetric measurements. The slowness of the transformation near the point of discontinuity, however, prevents usual calorimetric methods from being applied. It is possible that the determination will succeed by special methods now being tried out in our laboratory.*

VII.—Comparison with Approximations of Bragg and Williams, Bethe, and Others.

To the survey of our own investigation on the theory of equilibrium of the kinetics of order-disorder transformations, a few words may be added on the relation of our results to those of other investigators.

At about the same time as the paper describing the theory of equilibrium of transformations, summarized in equations (3), (4), and

* At the time of passing the proof of this paper in August 1947 preliminary results were obtained on the energy of transformation at 666° K. These results agree with the diagram of Fig. 1 (c).

(5), was published, there appeared an investigation on the same subject by Bragg and Williams. 14 The basic assumption as to the atomic interactions was more specialized than ours and, although formulated in another way, it has been shown by Bethe 15 to be consistent with the assumption that the energy is given exclusively by the number of pairs of nearest atoms of the types AA, BB, and AB. We, on the other hand, had left it to be decided by comparison with experimental results whether interactions between two, four, six, or more atoms were to be considered. Though the methods of discussion in our paper and in that of Bragg and Williams are at first sight rather different, a further analysis shows that all other essential assumptions are the same. Thus our conception of two interpenetrating lattice parts, to which the A- and B-atoms are referred in the ordered state, and the use of Boltzmann statistics on the assumption that there is a random distribution of Aand B-atoms within each lattice part, are tacitly understood by Bragg and Williams. They are more directly expressed in the paper of Bethe and in later works from this group of investigators. A difference between these investigators and us in the definition of degree of order is purely formal. The degree of order, S, used by Bragg and Williams, Bethe, and others is connected with the degree of disorder, q, used in the present paper by the formula S = 1 - 2q, S = +1, and S = -1, corresponding to q=0 and q=1, means full order; S=0, corresponding to q = 0.5, means full disorder. Thus the approximation of Bragg and Williams is a special case of our theory, obtained by making β, γ, &c., in the energy expression, equation (4), equal to zero. The U T curve according to Bragg and Williams was shown in Fig. 1 (a). It is rather different from all observed curves. A fairly large negative value of β seems to be essential for all experimental curves observed until now.

The possible influence of fluctuations on the state of order of small groups of atoms (order of neighbours) was first pointed out by Bethe, ¹⁵ who tried to obtain approximations to the partition function including this influence. This line of investigation has been continued by Kirkwood ¹⁶ and others. The statistical problem of computing the partition function has been found very difficult, even with the utmost simplification of the basic assumptions, and only considering interactions between pairs of neighbouring atoms. For the related problem of ferromagnetism, Onsager ¹⁷ seems to have succeeded in finding the general solution for a quadratic two-dimensional lattice. It must be emphasized, however, that even if solutions could be found for three-dimensional lattices on the basis of interactions of pairs, these solutions would probably not be able to describe real transformations in alloys.

The mathematical simplification of interactions in pairs, which was considered at an early stage in this discussion,2 has probably no physical meaning. There are arguments against it from the observed types of two-phase boundaries in alloy systems 11; and the great empirical values of the constant β in equation (4) indicate the necessity for taking into account the interactions in different groups of at least four atoms. For instance, in a binary alloy AB with close-packed structure one could expect the small tetrahedral elements of volume, which have the centres of four neighbouring atoms at their corners, to give different contributions to the energy for the different configurations A_4 , A_3B , A_2B_2 , AB_3 , and B_{A} .

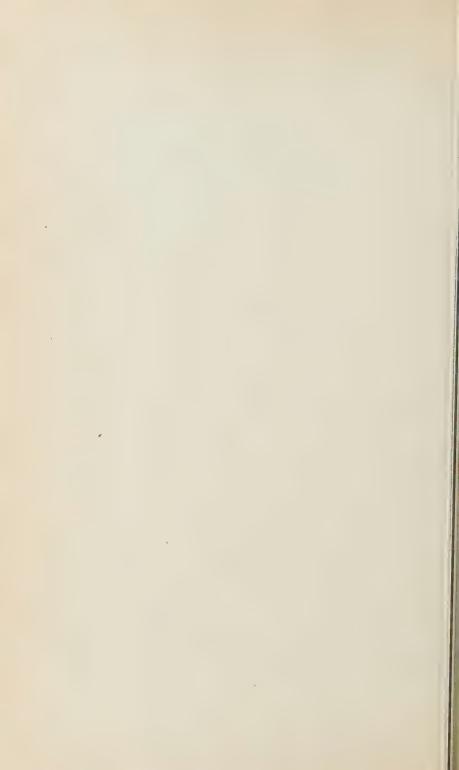
The theory of the kinetics of order disorder transformations was discussed to some extent by Bragg and Williams. They discussed the changes of place of individual atoms, and their results are confined to the first two factors τ_0 and exp. (W/RT) of equation (8). The third factor, which is dependent on the fluctuation of large groups of atoms, was not included in this discussion. Siegel 18 has carried out an interesting experimental investigation on the kinetics of transformation in Cu₃Au, using variations of the elastic moduli. He found a decrease in the rate of transformation slightly below the critical point, similar to that found by us in the case of AuCu. The phenomenon was qualitatively described by adding to the formula for the time of relaxation an empirical factor exp. $(L/R(T_c-T))$, where L is a constant and T_c the critical temperature. The results have not yet been analysed from the point of view of the fluctuation theory reported in section V.

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THE CONSTITUTION OF ALLOYS OF 1110 ALUMINIUM WITH COPPER AND MANGANESE.*

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Synopsis.

The constitution of the ternary alloys aluminium-copper-manganese, as slowly cooled, has been studied in detail by thermal and microscopic methods over the range copper 0-18, manganese 0-8%. The constituents present were found to be MnAl₄, MnAl₆, a(Cu-Mn), CuAl₂, and aluminium. Depending on the quantity of copper present, MnAl₄ reacts peritectically with the liquid to form either MnAl₆ or $\alpha(\text{Cu-Mn})$: MnAl₆ reacts peritectically with the liquid to form $\alpha(\text{Cu-Mn})$. The invariant points were found to be:

Point.	Phases Present.	Compos	Tem- pera-	
		Cu.	Mn.	ture, ° C.
Peritectic. } Ternary eutectic. {	$\begin{array}{l} \operatorname{MnAl_4}, \operatorname{MnAl_6}, \alpha(\mbox{`u-Mn}), \operatorname{Liq}. \\ \operatorname{Al}, \operatorname{MnAl_6}, \alpha(\mbox{`cu-Mn}), \operatorname{Liq}. \\ \operatorname{Al}, \alpha(\mbox{`cu-Mn}), \operatorname{CuAl_2}, \operatorname{Liq}. \end{array}$	15·75 14·85 32·5	2·20 0·90 0·60	625 616 547·5

In the primary aluminium field the liquidus temperature is extremely sensitive to changes in copper content and is practically unaffected by changes in manganese content; in the primary MnAl₄ field the converse is true; and in the primary MnAl₆ field the liquidus temperature is affected equally by changes in copper and manganese content.

When copper is added to 1.25% manganese alloys the solidus temperature is lowered: a(Cu-Mn) appears at 0.3% copper, at 616°C.

and CuAl₂ at 0.4% and 547.5° C. This may involve risk of hot-shortness.

Additions of manganese have very little effect on the structure of 4.0% copper alloys until the MnAl₆ field is entered at 1.6%, when there is risk of segregation.

I.—Introduction.

This investigation is one of a series 1 on the constitution of aluminium alloys under conditions of metastable equilibrium such as are likely to be met with in commercial practice.

There are only a few aluminium-rich alloys of this system which are important commercially. The addition of small quantities of manganese to binary aluminium-copper alloys as a means of improving their strength at high temperature has been suggested by Corson,2

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although he points out that these additions will impair the heat con ductivity of the alloys.3 However, little or no commercial application seems to have been made on these lines, and the alloys now in use fall into two main categories. One containing copper 3.9.5.0 with manganese 0·5-1·2% is used for forgings, 4 also in sheet form as ε general-purpose alloy of medium strength; and the other, containing copper 1.0-1.5 and manganese 0.7-1.2%, is used for sand castings.5

Quaternary and more complex alloys containing aluminium, copper and manganese are, of course, in widespread use-Duralumin migh be mentioned as an important example—and in investigating the structure of these complex alloys it is necessary to know something of the constitution of the ternary systems involved, since binary and ternary constituents of the simpler systems may persist in the presence

of other alloying additions.

Manganese may be present as a contaminant in cast and wrough! aluminium-copper alloys, and similarly copper may occur in binary aluminium manganese alloys: a knowledge of the ternary system is therefore helpful in fixing the limits within which such contaminants may be permissible commercially.

II.—Scope of the Investigation.

The work completed in this laboratory 6 some years ago on the aluminium-rich end of the aluminium-copper binary system agrees substantially with that published by Raynor, and the binary system aluminium-manganese is now well established; 8 so no further world was undertaken on the binary systems.

It was decided to study the range copper 0-18, manganese 0-8% in detail, though a few cooling curves were carried out in the range copper 20, manganese 0-8%, and some alloys were studied in the neighbourhood of the ternary eutectic covering a range copper 30-35 manganese 0-2.0%.

The alloys were made up from super-purity aluminium (99.992%) The copper and manganese were added in the form of hardeners containing approximately 50 and 20%, respectively, of the alloving element. The detailed analysis of the hardeners was as shown in Table I

TABLE I.

	Mn.	Cu.	Si.	Fe.
Manganese hardener, %	19.6	0.0015	0·0045	0·0020
	<0.01	50.0	0·003	0·0025

The detailed analysis of some of the alloys given in Table II indicates the order of the quantities of impurities actually present in the alloys studied.

TABLE II.

Nominal Composition, %.		Detailed Analysis, %.					
Cu,	Mn.	Cu.	Mn.	Si.	Fe.		
8 16 16	5 5 8	7·85 15·7 15·9	5·00 5·1 7·8	0·0025 0·0020 0·0015	0·0020 0·0020 0·0025		

Cooling curves were taken on samples weighing 200 g., and the ingots were afterwards sectioned for microscopic examination. The rate of cooling was in general about 4°-7° C. per minute, though slower and faster rates were employed on occasion. Temperatures were measured by a platinum/platinum-rhodium thermocouple used in conjunction with a Carpenter-Stansfield potentiometer. In the cases where ingots were to be analysed they were remelted and chill cast before analysis to minimize errors due to segregation of manganese-rich constituents.

Copper, if present in amounts of less than 18%, was determined volumetrically by means of thiosulphate.9 For alloys in the neighbourhood of the ternary eutectic, containing amounts of copper of the order of 32%, the electrolytic method was used. 10 Where copper was present only as a minor impurity, as in super-purity aluminium and certain of the hardener alloys, the estimation was made by the colorimetric method based on the use of sodium diethyldithiocarbamate. 11 Manganese, in general, was estimated photometrically by the periodate process, 12 the figures being confirmed by the volumetric process involving sodium bismuthate as oxidant. 13 If present only as a minor impurity, manganese was determined colorimetrically, potassium periodate being used as the oxidant and the colour matched visually against appropriate standards. 14 Silicon and iron were present only as incidental impurities. Both were estimated colorimetrically, the former by matching the yellow colour developed by ammonium molybdate in acid solution against standard picric acid, 15 and the latter, after removal of the copper, by the thiocyanate process. 16

III.—HISTORICAL SURVEY.

The constitution of alloys belonging to the aluminium-rich corner of this system was first studied by Rosenhain and Lantsberry ¹⁷ who

identified an aluminium-rich compound, which they called MnAl₃, but gave no details of the ternary structure. Krings and Ostmann ¹⁸ used thermal and microscopic methods to investigate the constitution of the system; they identified no ternary compound, and concluded that the phases MnAl₄, CuAl₂, and aluminium formed a ternary eutectic of composition copper 29·6, manganese 3%, freezing at 536° C.

Sawamoto ¹⁹ investigated the system over the range copper 0–40, manganese 0–3%, employing differential thermal analysis and microscopic methods. He reported the occurrence of a peritectic reaction resulting in the formation of MnAl₃ and aluminium at a temperature of 630° C. and a composition of copper 8·3, manganese 1·75%. The ternary eutectic of copper 30·5, manganese 0·65% froze at 544° C., and contained the phases MnAl₃, CuAl₂, and aluminium.

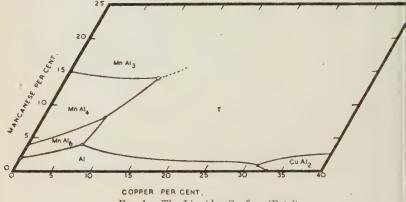


Fig. 1.—The Liquidus Surface (Petri).

Petri ²⁰ used thermal and microscopic methods to make a study of the alloys over the range copper 0-45, manganese 0-17%. The alloys were prepared from aluminium of 99·996% purity, electrolytic copper, and anhydrous manganese chloride, and were studied as slowly cooled and also after prolonged annealing. His liquidus surface is shown in Fig. 1; and his 500° C. isotherm indicating the phases present in alloys which had been annealed in a vacuum for 14 days at 500° C. and then quenched in water, is shown in Fig. 2. The phases present were aluminium containing copper and manganese in solid solution (Al), MnAl₆, MnAl₄, MnAl₃, and the ternary phases "T" and "Y"; he did not investigate the latter ternary phase in detail. "T" was a phase of variable composition; its homogeneity limits, under conditions of equilibrium at 500° C., extending between the compositions indicated by the points "T₁" and "T₂" in Fig. 2. As Raynor ²¹ has

pointed out, "T" appears to be based on the composition ('u₂Mn₃Al₂₀. The point *P* corresponding to this composition has been inserted in Fig. 2, and, as will be seen, lies in close proximity to Petri's point "T₂". The phases Al, CuAl₂, and "T" formed a ternary eutectic containing copper 31·5 and manganese 0·8%, and freezing at 547·3° C. Three peritectic invariant reactions occurred, but owing to undercooling and segregation their temperatures could not be determined accurately.

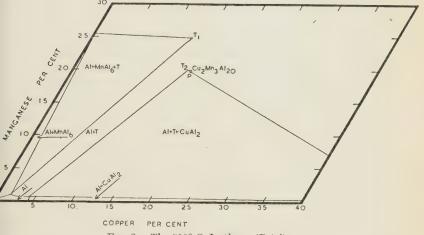


Fig. 2.—The 500° C. Isotherm (Petri).

The constituent "T," extracted from an alloy in which it was primary, was examined by X-rays and found to crystallize in the orthorhombic system (a=7.69, b=24.06, c=12.48 Å), the particular crystal examined having the composition copper 19 and manganese 24%. The constituent "Y" occurred in alloys rich in copper and manganese, and was also found to be orthorhombic (a=14.79, b=12.60, c=12.43 Å).

Mondolfo ²² has also studied the system. His liquidus surface showed a continuous phase field, (Cu,Mn)Al₄, extending from the MnAl₄ field on the manganese axis across to the eutectic. He found that the ternary eutectic point had the same composition and melting point as reported by Petri, but concluded that the phases present were Al-(CuMn)Al₄-CuAl₂. Since he did not identify any distinct ternary body the only peritectic reaction between MnAl₄ and the liquid which

he reported was that which results in the formation of MnAl₆: this was limited to alloys in which the copper content did not exceed 19%.

Guertler and Rassmann ²³ employed X-rays to study the constitution of alloys of the system under equilibrium conditions and confirmed Petri's ²⁰ diagram as regards phase fields. They reported that the sections MnAl₆-"T", Al-"T", and CuAl₂-"T" were quasibinary.

IV .- MICROGRAPHY OF THE ALLOYS.

Within the range of compositions studied, copper 0-18 and manganese 0-8%, five phases were identified. They may be listed as follows:

- (a) Aluminium. This forms the continuous phase in all the alloys investigated. It contains some copper and manganese in solid solution, the amount depending on the conditions of cooling during solidification and subsequently. Variation in the copper content from the centre to the exterior of the aluminium crystallites was sufficient to give rise to visible coring on etching with dilute sodium hydroxide solution or hydrofluoric acid. It would be expected that both copper and manganese would be rejected from solid solution during cooling below the solidus, and that on examination under the highest powers of the microscope it would be possible to detect fine particles of a highly dispersed phase in the aluminium crystallites; but no such particles could be detected.
- (b) $MnAl_6$. This constituent retains, in the ternary alloys, the characteristic crystal habit which it exhibits in the binary alloys of aluminium and manganese. Hoffmann 24 examined the crystals by X-rays, and found that they crystallized in the orthorhombic system (a = 6.51, b = 7.57, c = 8.87 Å). The crystals are regular in outline, dendritic in habit, and frequently hollow. They are purplish-pink in colour, and are only lightly attacked by dilute sodium hydroxide solution or hydrofluoric acid. They are frequently surrounded by a sheath of the reaction product $\alpha(Cu-Mn)$: where the reaction has taken place in the presence of the liquid phase, the MnAls shows the usual indented appearance characteristic of peritectic attack, but where it has taken place by diffusion in the solid the outlines are smoother. the a(Cu-Mn) being pseudo-morphic after the MnAl6. The boundary between MnAl₆ and $\alpha(Cu-Mn)$ is sometimes difficult to distinguish in the unetched state, but can readily be rendered visible by etching for 1½ minutes in 20% nitric acid at 70° C., the etch giving the reaction product a distinct brownish tinge, shown in half-tone in Fig. 3 (Plate

IX). According to Raynor ²¹ MnAl₆ is practically incapable of taking any copper into solid solution.

(c) MnAl₄. This constituent occurs as cores in duplex crystals, the sheath being either MnAl₆ or $\alpha(Cu-Mn)$, or as the inner core in triplex crystals $MnAl_4-MnAl_6-\alpha(Cu-Mn)$. It is purplish-pink in colour, though the colour is less pronounced than that of MnAl₆. The MnAl₄ cores are roughly hexagonal in outline, showing marked signs of peritectic attack, and often contain central cavities in the form of 6-rayed stars. The boundaries between MnAl4 and its sheath are extremely difficult to distinguish in unetched specimens, whatever the nature of the sheath, particularly if relief effects have not developed during the final polishing. Etching with 20% nitric acid at 70° C. serves to render visible the boundary between MnAl₄ and MnAl₆ or α(Cu Mn) in duplex crystals; and that between MnAl₄ and α(Cu-Mn), but, strangely enough, not that between MnAl₄ and MnAl₆, in triplex crystals. For these crystals, a second etch is necessary: with a few seconds' immersion in 12.5% sodium hydroxide solution the inner boundary MnAl4-MnAl, is well developed, and the MnAl, darkened (Fig. 4, Plate IX). An example of a duplex crystal MnAl₄-α(Cu-Mn) is shown in Fig. 5 (Plate X).

Hoffmann ²⁴ has shown that MnAl₄ crystallizes in the hexagonal system (a=28.35, c=12.36 Å).

(d) $\alpha(Cu-Mn)$. This constituent, termed "T" by Petri,²⁰ is a phase of variable composition. According to Petri two of the apices of the concentration area representing its homogeneity range are the points "T₁" (Cu 13, Mn 24·9%) and "T₂" (Cu 15, Mn 20%), indicated in Fig. 2. In the present investigation the composition of $\alpha(Cu-Mn)$ which fitted the experimental results best was found to be copper 19, manganese 24%: this agrees with the composition of the sample of "T" which Petri extracted and on which he made his X-ray measurements. Over a certain range of compositions $\alpha(Cu-Mn)$ separates directly from the melt: elsewhere it occurs as the product of a peritectic reaction between MnAl₄ or MnAl₆ and the liquid. It is more counded in outline than either MnAl₄ or MnAl₆, and is rather darker in colour in the unetched state. Its characteristic crystal form is shown in Fig. 6 (Plate X). It is isomorphous with the ternary phases $\alpha(Mn-Si)$ and $\alpha(Fe-Si)$.²⁵, ²⁶

(e) $CuAl_2$. This designation has become established by long usage and will therefore be retained, although, as Stockdale ²⁷ has shown, an alloy of which the composition corresponds with the formula lies ust outside the region of homogeneity of the phase. It has been ound from X-ray investigation that CuAl₂ crystallizes in a body-

centred tetragonal structure with 8 Al and 4 Cu atoms per unit cell $(a=6.05,c=4.86\mbox{ Å}).^{28,29,30}$ Over the range of compositions studied, $(\mbox{`uAl}_2$ appears only as one of the constituents of the ternary eutectic. In the unetched state it is pale pink in colour, and it is readily identified by its reaction with the hot nitric acid etch, which blackens it. Raynor 21 has shown that it is practically incapable of dissolving any manganese.

V.—THE LIQUIDUS SURFACE.

The liquidus surface is shown in plan in Fig. 7. It is composed of four primary phase fields:

Aluminium				ABCKH
MnAl ₆ .				HKLG
a(Cu-Mn)				KCDL
MnAl.				GLDEF

The primary aluminium field is bounded by the $\operatorname{MnAl_6}$ -aluminium eutectic valley HK and the $\alpha(\operatorname{Cu-Mn})$ -aluminium eutectic valley KC; beyond the range of composition studied the valley KC runs down to the ternary eutectic point T, and the remaining side of the field is closed by the $\operatorname{CuAl_2}$ -aluminium eutectic valley.

The temperature and composition corresponding with the ternary eutectic point T were deduced from cooling-curve arrests and the examination of a number of micro-sections of slowly cooled alloys of compositions within the range copper 30–35 and manganese 0.25-2.0%, the best estimate being copper 32.50 and manganese 0.60% at a temperature of 547.5° C. It was found that the eutectic was so segregated that analysis of an apparently all-eutectic area would have been misleading.

The primary $\operatorname{MnAl_6}$ field is separated from the $\operatorname{MnAl_4}$ and $\alpha(\operatorname{Cu-Mn})$ fields by the lines GL and LK , respectively, each of which is associated with a peritectic reaction. GL is associated with the peritectic reaction between $\operatorname{MnAl_4}$ and the liquid to form $\operatorname{MnAl_6}$, and LK that between $\operatorname{MnAl_6}$ and the liquid to form $\alpha(\operatorname{Cu-Mn})$.

The compositions and temperatures corresponding with the invariant points K and L were determined by interpolation from the phase boundaries and from the liquidus isothermals, and are shown in Table III.

The only boundary of the $\alpha(\text{Cu-Mn})$ field which has not yet been mentioned is DL: this is associated with the peritectic reaction between MnAl₄ and the liquid to form $\alpha(\text{Cu-Mn})$.

It is interesting to note that the atomic percentages of points lying on the isothermals of the MnAl₄ field, when plotted on a log-log



Fig. 3. —MnAl $_6$ Partly Surrounded by a(Cu-Mn) in Slowly Cooled Alloy Containing Copper 8·0 and Manganese $3\cdot0\%$. (No MnAl $_4$ present, due to undercooling.) Specimen etched $1\frac{1}{2}$ min. in 20% HNO $_3$ at 70° C. \times 150.



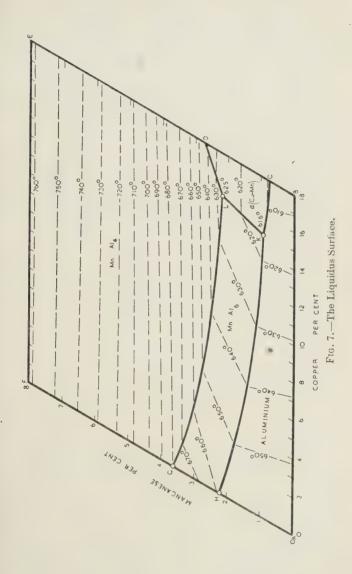
Fig. 4.—Triplex Crystals of MnAl, Core in MnAl, Surrounded by α (Cu–Mn) in Slowly Cooled Alloy Containing Copper 8·0 and Manganese 4·0%. Specimen etched $1\frac{1}{2}$ min. in 20% HNO $_3$ at 70° C., followed by dip in cold $12\cdot5\%$ NaOH. \times 175.



Fig. 5.—MnAl $_4$ Surrounded by a(Cu–Mn) in Slowly Cooled Alloy Containing Copper 14 and Manganese 8.0%. Specimen etched 1 $_2$ min. in 20% HNO $_3$ at 70° C. \times 150.



Fig. 6.—Primary Crystals of $\alpha(Cu-Mn)$ and Eutectics Area in Slowly Cooled Alloy Containing Copper 20 and Manganese $2\cdot0\%$. Specimen etched 20 sec. in 20% HNO3 at 70° C. \times 150.



scale, do not conform with a gradient of 1:4 as might have been expected from the Law of Mass Action. The 750° C. isothermal has been plotted in this manner in Fig. 8 and might lead one to suppose, from its slope, that the compound separating contains manganese and aluminium in equal atomic proportions.

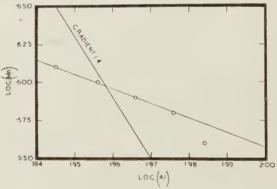
TABLE III .- Ternary Invariant Points: Liquid Surface.

Point.	Phases Present.	Compos	Temperature,	
		Copper.	Manganese.	0.
K L T	Al, MnAl ₆ , α (Cu–Mn), Liq. MnAl ₄ , MnAl ₆ , α (Cu–Mn), Liq. Al, α (Cu–Mn), CuAl ₂ , Liq.	14·85 15·75 32·50	0.90 2.20 0.60	616 625 547·5

The Le Chatelier 31 form of the equation connecting the apparent solubility product K of an intermetallic phase with temperature is:

$$\operatorname{Log} K = \frac{\Delta H}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)$$

where ΔH is the difference in heat content between reactant and resultant, and includes the heat of formation and the latent heat of



750 °C Isothermal of the Primary Mn Al₄ Field.

Fig. 8.

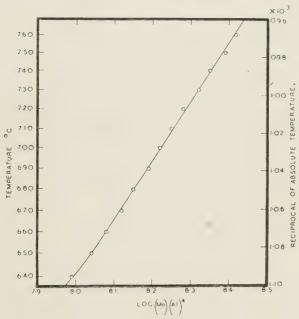
fusion of the compound concerned; T_0 is the freezing point of the pure substance, T is the operating temperature, and R the gas constant.

Fig. 9 shows the application of this equation to the liquidus isothermals of the primary $MnAl_4$ field. It will be seen that the graph is linear over a wide range of temperature; the value of ΔH calculated

from the slope of the graph was found to be 1.49×10^4 cal./g. mol, which is equal to 91.7 cal./g.

The intersections of the liquidus isothermals with the univariant lines comply in all cases with the Lipson-Wilson ³² rules for ternary equilibria.

It may be noted that in the primary aluminium field the liquidus



Variation of the Apparent Solubility Product with Temperature,

Fig. 9.

sothermals run practically parallel to the manganese axis, so that additions of manganese have no appreciable effect on the liquidus emperature, whereas this temperature is extremely sensitive to changes in copper content. In the primary MnAl₆ field, variations in the opper and manganese content have equal effects on the liquidus emperature, and in the primary MnAl₄ field, the isothermals run tractically parallel to the copper axis so that the liquidus temperature is very sensitive to changes in the manganese content and is unaffected by changes in the copper content.

The above-mentioned points are important when considering the ossible compositions of hardener alloys; it will be seen that in the $InAl_4$ field the liquidus temperature rises very rapidly with small

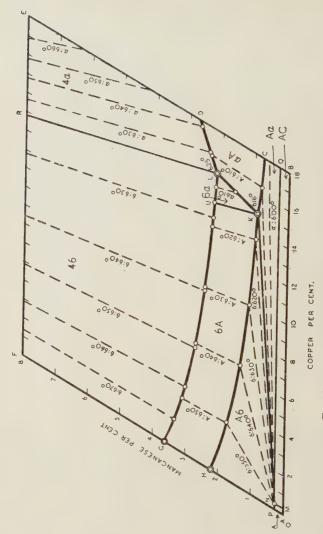


Fig. 10.—Secondary Separations. Alloys as slowly solidified.

increases of manganese, so that close analytical control of this element would be essential.

VI.—REACTIONS BELOW THE LIQUIDUS.

The surfaces of the secondary and later separations are shown in plan in Figs. 10 and 10 (a). The key to the symbols used is given in Table IV.

Table IV.—Symbols Used in Figs. 10-16.

- Aluminium
- MnAl₄ MnAl₆
- $\begin{array}{cc} \alpha & \alpha(\mathrm{Cu-Mn}) \\ C & \mathrm{CuAl_2} \end{array}$
- L Liquid

The order of crystallization of phases is indicated by the order in which the symbols are written.

dotted isothermals; ternary separation.

dashed isothermals; secondary separation.

The first symbol written along the isotherma represents the constituent separating, the second the temperature.

There are three main secondary fields associated with the primary aluminium field ABCKH, the dividing lines being NK, NM, and NQ, the last of which runs down to the ternary eutectic point T. In addition, there is the area AMNP, which represents the limits within which the solid solution of copper and manganese in aluminium is the only constituent present under the conditions of cooling employed in the present investigation. In the field PNKH, the secondary separation is that of the aluminium-MnAl, binary complex. This may be sub-divided into three subsidiary fields. If the copper content of the alloy is very small—as in alloys lying to the left of the line NZ—solidification will be completed during this stage; if the copper content is higher the secondary separation of aluminium and MnAl will continue until the temperature has fallen to 616° C. At this point the peritectic reaction which results in the formation of $\alpha(Cu-Mn)$ takes place; this reaction does not usually proceed to completion, and the alloys often contain a fair amount of residual MnAl6. Freezing continues with the separation of the aluminium-\alpha(Cu-Mn) complex; in the case of alloys of compositions lying in the field marked $A6\alpha$ in the figure, solidification is completed during this stage; if solidification is not completed the separation will continue until the temperature has fallen to that of the ternary eutectic (547.5° C.).

In the field NQCK, the secondary separation is that of the aluminium-α(Cu-Mn) complex, and this will continue until the temperature has fallen to that of the ternary eutectic. In the field MBQN, the aluminium-CuAl2 binary complex is secondary; if the manganese content of the alloy is very small—as in alloys lying below the line NX—solidification will be completed during this stage, but if the manganese content is greater than 0.2% the secondary separation will continue until the temperature has dropped to that of the ternary eutectic.

The primary MnAl6 field has associated with it two secondary fields separated by the line KU. The tie lines in these fields are consistent with the calculated composition of MnAl₆, i.e. 25.35% manganese. In the concentration area HKUG the secondary separation is that of aluminium; if the copper content of the alloy is very small solidification may be completed at this stage, otherwise the separation will proceed along the binary valley HKCT, and the course of solidification will be as described for alloys in the field PNKH. In the concentration area KLU the secondary separation is that of α(Cu-Mn), formed as the result of the peritectic reaction between MnAl, and the liquid. As is general in aluminium alloy systems, the peritectic reaction does not proceed to completion, but ceases as soon as the primary constituent (MnAl₆) has become completely enveloped in a sheath of reaction product. When this happens, the point on the diagram representing the composition of the liquid phase leaves the phase boundary KL, and moves across the field of the $\alpha(Cu-Mn)$ phase, reaching the eutectic valley at some point to the right of the point K. The tie lines in this field are consistent with the findings. of Petri ²⁰ that α(Cu-Mn) can have the approximate composition copper 19 and manganese 24%. When the eutectic valley is reached. aluminium commences to separate in its binary complex with α(Cu-Mn). and solidification proceeds until the ternary eutectic point T is reached.

Alloys lying in the concentration area KCDL have $\alpha(Cu-Mn)$ as their primary, aluminium as their secondary, and $CuAl_2$ as their ternary constituent.

There are two secondary-phase fields associated with the primary $\operatorname{MnAl_4}$ field. The tie lines in these fields are consistent with the calculated values of the composition of $\operatorname{MnAl_4}$ and $\operatorname{MnAl_6}$, i.e. 33·72 and 25·35% manganese, respectively. In the area GLRF the secondary separation-is that of $\operatorname{MnAl_6}$ which is formed as a result of the peritectic reaction between $\operatorname{MnAl_4}$ and the liquid: as this reaction rarely proceeds to completion, the alloys almost invariably contain some residual $\operatorname{MnAl_4}$. Later separations proceed in the manner described for the $\operatorname{MnAl_6}$ primary field; in the area GUSF aluminium is the ternary constituent, and in the area ULRS $\alpha(\operatorname{Cu-Mn})$ is ternary. In the field LDER the secondary separation is $\alpha(\operatorname{Cu-Mn})$ formed by the peritectic

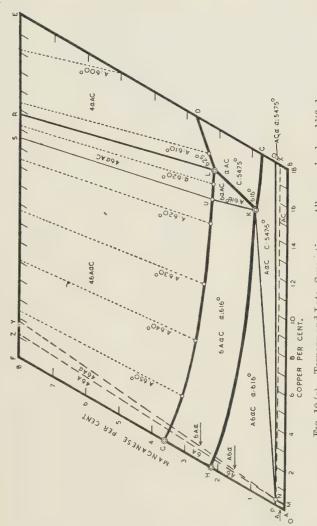


Fig. 10 (a).—Ternary and Later Separations. Alloys as slowly soldified.

reaction between MnAl₄ and the liquid, again the reaction rarely proceeds to completion and the alloys often contain some residual MnAl₄; the ternary constituent is aluminium, and CuAl₂ the quaternary one.

VII.—CONSTITUENTS PRESENT IN THE SOLID STATE.

The limits of occurrence of the various phases under the conditions of cooling employed in the investigation are shown in Fig. 10 (a).

The area AMNP represents the limits of occurrence of singlephase alloys, the aluminium-rich solid solution alone being present.

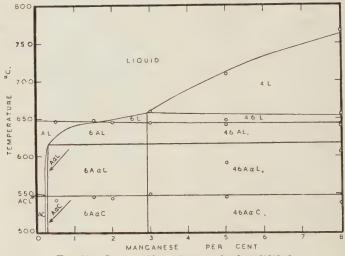


Fig. 11.—Copper 4%. Alloys as slowly solidified.

 α (Cu-Mn) is to be found in all alloys lying to the right of the dotted line MNZ and above the dotted line PNX. CuAl₂ occurs in all alloys other than those in the area lying to the left of the line MNY. The peritectic line GLD marks the lower limit of occurrence of MnAl₄, while MnAl₆ occurs in all alloys lying within the area PNKLRF.

VIII.—SECTIONAL DIAGRAMS.

Six diagrams, Figs. 11-16, have been included. They show the constitution of series of alloys containing 4, 8, and 16% copper, and 5, 8, and 1.25% manganese, respectively. The only sections which call for detailed comment are those of the series of alloys containing 4% copper and 1.25% manganese.

When a small quantity of manganese is present as an impurity in

E

a 4% copper alloy, no manganese-bearing phase appears until the amount of manganese has reached 0.2%, and there is no appreciable change in the temperature of the liquidus and solidus of the alloy until manganese 1.6% is present. At the latter composition, the MnAl₆ field is entered, and risk of segregation becomes pronounced.

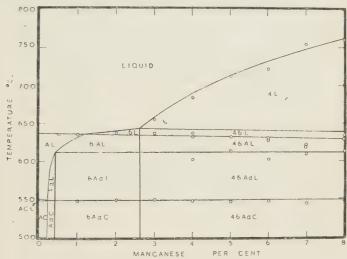


Fig. 12.—Copper 8%. Alloys as slowly solidified.

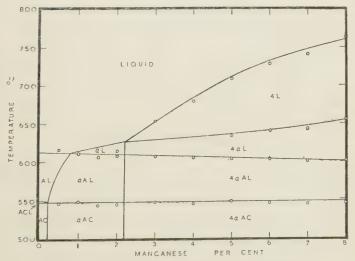


Fig. 13.—Copper 16%. Alloys as slowly solidified. VOL, LXXIV.

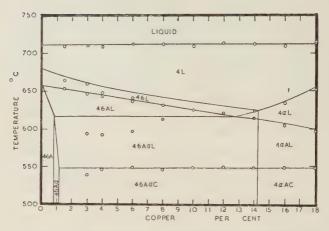


Fig. 14.—Manganese 5%. Alloys as slowly solidified.

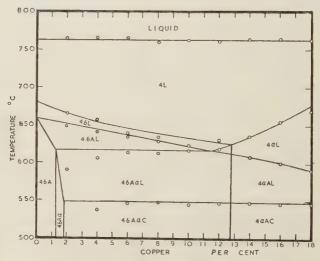


Fig. 15.—Manganese 8%. Alloys as slowly solidified.

In the case of 1.25%-manganese commercial alloys, the effect of adding copper is to lower the solidus temperature: the solidus slopes down steeply to the $\alpha(\text{Cu-Mn})$ arrest, and still more steeply to the CuAl_2 arrest, reaching the ternary eutectic temperature in the latter case. This may involve risk of hot-shortness. The first appearance of a copper-bearing phase $\alpha(\text{Cu-Mn})$ occurs at copper 0.3%, and CuAl_2

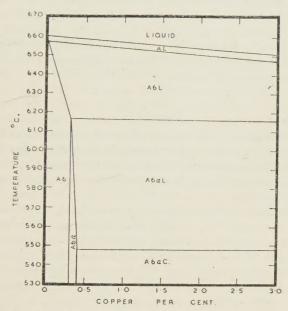


Fig. 16.—Manganese 1·25%. Alloys as slowly solidified.

tself appears at copper 0.4%. Annealing at a high temperature would cause copper to be taken into solution, thereby raising the solidus temperature and reducing the tendency to hot-shortness.

IX.—STRUCTURE OF ALLOYS AS ANNEALED.

A preliminary investigation of alloys of which the composition ay within the range copper 0-5·0 and manganese 0-0·75%, annealed t 500° C. and quenched, showed that very prolonged annealing times would be needed to ensure equilibrium even at relatively high temperatures, and that it would be a matter of considerable difficulty to etermine accurately the positions of the various phase boundaries. The new aluminium-rich phase which Little, Raynor, and Hume-Rothery 33 have called "G" was identified in a number of micro-

sections, but was difficult to distinguish from $\alpha(\text{Cu-Mn})$. No chemical etch has yet been found which will satisfactorily discriminate between these two constituents, and electrolytic etching, whilst very suitable for revealing minute quantities of a precipitated phase, tends to give a variety of colours on any of the manganese-bearing constituents, and so is unreliable as an aid to their identification. Little, Raynor, and Hume-Rothery showed that a limited quantity of "G" was present in binary aluminium-manganese alloys even after a prolonged period of annealing (40 days at 550° C.), and that it appears to be a metastable phase. Work on the ternary alloys, which is still proceeding, suggests very strongly that similar conditions of metastability persist in the presence of copper.

SUMMARY.

The constitution of the ternary alloys of aluminium with copper and manganese as slowly cooled was studied in detail over the range copper 0–18 and manganese 0–8%, by thermal and microscopic methods, but a few additional alloys were examined in the neighbourhood of the ternary eutectic.

The constituents present were found to be MnAl₄, MnAl₆, a ternary complex called $\alpha(\text{Cu-Mn})$, CuAl_2 , and aluminium. The last three form a ternary eutectic containing copper 32·5 and manganese 0·6%, and freezing at 547·5° C. Depending on the quantity of copper present, MnAl₄ reacts peritectically with the liquid to form either MnAl₆ or $\alpha(\text{Cu-Mn})$, and MnAl₆ also reacts peritectically with the liquid to form $\alpha(\text{Cu-Mn})$; these peritectic reactions rarely proceed to completion, and in the solid alloys of suitable composition, residual cores of MnAl₄ or MnAl₆, or both, can be detected in the crystals of MnAl₆ and $\alpha(\text{Cu-Mn})$. The invariant point at which MnAl₄, MnAl₆, and $\alpha(\text{Cu-Mn})$ are in equilibrium with the liquid lies at copper 15·75 and manganese $2\cdot20\%$ at a temperature of 625° C., and that at which aluminium, MnAl₆, $\alpha(\text{Cu-Mn})$, and the liquid are in equilibrium lies at copper 14·85 and manganese $0\cdot90\%$ and 616° C.

In the primary aluminium field the liquidus isothermals run practically parallel to the manganese axis; in the MnAl₆ field variations in the copper and manganese content have equal effects on the liquidus temperature, and in the MnAl₄ field the liquidus isothermals run parallel to the copper axis. There is no metallurgical objection to the use of ternary alloys as hardeners, but owing to this relationship between manganese content and liquidus temperatures, critical analytical control will be needed. The intersections of the liquidus isothermals

with the univariant lines comply with the Lipson-Wilson rules for ternary equilibria. The atomic percentages of points lying on the isothermals of the MnAl₄ field, when plotted on a log-log scale, do not conform with a gradient of 1:4 as might have been expected from the Law of Mass Action. When the Le Chatelier form of the equation connecting the apparent solubility product of an intermetallic phase with temperature is applied to the liquidus isothermals of the primary MnAl₄ field the graph obtained is linear over a wide range of temperature.

The tie lines of the various phase fields plotted are consistent with the calculated values of the composition of MnAl₄ and MnAl₆, i.e. 33·72 and 25·35% manganese, respectively, and with a value of the com-

position of α(Cu-Mn) of copper 19 and manganese 24%:

The boundary between the primary aluminium and MnAl₆ fields slopes towards the aluminium–copper axis; primary MnAl₆ appears at 1.6% manganese in commercial 4.0%-copper alloys: this point is important, since alloys in the primary MnAl₆ field are liable to segregation. In 1.25%-manganese commercial alloys small additions of copper lower the solidus temperatures of the alloys considerably, and this may involve the risk of hot-shortness: an addition of as little as 0.4% is sufficient to bring the temperature of final solidification down to that of the ternary eutectic, 547.5° C.

Very little work has yet been done on the structure of the alloys as annealed as, owing to the presence of a metastable phase "G", it was found to be impossible to reach equilibrium within a reasonable period of time, and difficulty has also been experienced in identifying the phases.

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